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United States
Environmental Protection
Agency

Office of Air Quality
Planning and Standards
Research Triangle Park NC 27711

EPA-450/3-81-004
April 1981

Air

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Control Techniques for Sulfur Oxide Emissions from Stationary Sources

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Second Edition

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EPA-450/3-81-004

Control Techniques for Sulfur Oxide Emissions from Stationary Sources

Second Edition

by

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

April 1981

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SECTION 1

INTRODUCTION

The first edition of "Control Techniques for Sulfur Oxide Air Pollutants" was published in January 1969.[1] The many changes and advances in sulfur oxide emission control technology, as well as changes in fuel use patterns since that time, have rendered many parts of the original document obsolete. This second edition contains up-to-date information on available control techniques, including cost, energy requirements, and environmental impact of sulfur oxide control technology, as required in Section 108(b) (1) of Public Law 91-604 of the Clean Air Act as amended August 7, 1977.

Sulfur oxides in the atmosphere are known to have many adverse effects upon health and welfare, and reduction of emissions of this class of pollutants is of prime importance to any effective air pollution abatement program. Sulfur oxide pollutants originate from a variety of sources, and the emissions vary widely in concentration and characteristics. Similarly, the available control techniques vary in type, application, effectiveness, and cost. The term "sulfur oxides" will be used when discussing emissions in general, and "SO_2" will be used when referring to sulfur dioxide specifically. Sulfur oxides are emitted mainly as sulfur dioxide (SO_2) and to a lesser extent as sulfur trioxide (SO_3), sulfuric acid mist (H_2SO_4), and sulfates. This document deals mainly with sulfur dioxide emissions control.

As in the first edition, the control techniques described herein represent a broad spectrum of information from many engineering and other technical fields. Many of the emission control devices, methods, and principles have been developed and used over several years, and much experience has been gained in their application. Discussions of methods still in various stages of research and development are included to provide information about the latest concepts under consideration, even though they are not yet available for general use.

The many commercial, industrial, and municipal processes and activities that generate sulfur oxide air pollutants are described individually. The various techniques that can be applied to control emissions of sulfur oxides from these sources are reviewed and compared. No attempt is made, however, to review all possible combinations of control techniques that might bring about more stringent control of each individual source.

The proper choice of a method, or combination of methods, to be applied to any specific source depends on many factors in addition to the characteristics of the emission stream. State or local governments may impose additional emission restraints; control regulations may also depend on relative distance to a Class I Air Quality Control Region, whether the area is a nonattainment area, and other considerations.

Some data are presented on quantities of sulfur oxides emitted to the atmosphere; the effects of sulfur oxides on health and welfare are considered in a companion document, "Air Quality Criteria for Sulfur Oxides."[2]

Periodically the EPA publication "Compilation of Air Pollutant Emission Factors" (AP-42) is referred to in this document. The user of AP-42 should be aware that it is constantly being updated as new test data become available; therefore, the reader must be certain to utilize the most recent version of AP-42.

The general organization of this report is as follows. Section 2 discusses the characterization and sampling methods for sulfur oxides. Section 3 presents information on energy use patterns, determination of emission reduction needs, technical considerations, environmental and energy impacts of sulfur oxide control, and the sulfur products market. Sections 4 and 5 present information on the combustion process and industrial process emissions of sulfur oxides respectively. These two chapters are presented in the following sequence:

- Process description and emissions
- Control techniques
- Control costs
- Energy and environmental impacts.

The costs discussed in this document are in mid-1979 dollars unless specifically noted otherwise. Because of its wide applicability, the Chemical Engineering plant cost index was used to update costs. A mid-1979 value of 236.5 was used. The Chemical Engineering index is given in every issue of Chemical Engineering, a magazine published biweekly by McGraw-Hill, Inc., of New York, New York.

This document was prepared primarily from information on sulfur oxide emissions found in the open literature and was supplemented by personal contacts.

REFERENCES FOR SECTION 1

1. U.S. Department of Health, Education, and Welfare. Control Techniques for Sulfur Oxide Air Pollutants. Public Health Service. AP-52. January 1969.

2. U.S. Department of Health, Education, and Welfare. Air Quality Criteria for Sulfur Oxides. Public Health Service. AP-50. April 1970. (Document presently being revised.)

SECTION 2

THE SULFUR OXIDES: CHARACTERIZATION AND SAMPLING METHODS

This chapter addresses how SO_x are formed, the trends of sulfur oxide emissions, and both ambient and stack sampling equipment for measurement of sulfur oxides.

2.1 CHARACTERIZATION OF SULFUR OXIDES

This section briefly defines and characterizes the sulfur oxides and the reactions in which they are formed. Major sources and their contributions to nationwide SO_x emission totals are discussed.

Approximately 95 percent of the total pollution-related sulfur oxide emissions is in the form of sulfur dioxide, most of the remainder being sulfur trioxide, small amounts of sulfuric acid mist, and sulfates.[1,2]

2.1.1 Sulfur Dioxide

The primary source of SO_2 is combustion of fuels that contain sulfur. During combustion, atmospheric oxygen combines with the sulfur in the following reaction:

$$S + O_2 \rightarrow SO_2$$

Sulfur dioxide is a colorless, nonflammable acidic gas. The odor threshold for sulfur dioxide is 0.3 to 1.0 part per million (ppm) by volume; at concentrations above 3 ppm the odor is pungent.[3]

Formation of SO_2 occurs early in the primary flame at rates comparable with the other combustion reactions. Formation will occur even in fuel-rich flames; no practical combustion control techniques have been identified.[2] The degree of photochemical or catalytic conversion of SO_2 into its derivatives depends on atmospheric conditions such as humidity, catalytic sites, concentrations of hydrocarbons, and particulate matter composition in an effluent gas stream or in the atmosphere. The reaction kinetics of SO_2 in the atmosphere are outlined in a literature review (through 1970) by Bufalini.[4]

2.1.2 Sulfur Trioxide

Sulfur trioxide (SO_3) is formed from combustion sources directly or from oxidation of atmospheric SO_2 as follows:

$$SO_2 + 1/2O_2 \xrightarrow{\text{catalyst}} SO_3$$

Limitations in the chemical kinetic rates are such that only from 1 to 5 percent of the sulfur in the stack gases is observed in practice to be present as SO_3.[2] Sulfur trioxide is highly hygroscopic and normally combines with water vapor in the stack to form sulfuric acid as a finely divided aerosol:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Formation of SO_3 is found to occur only in air-rich mixtures and to be governed by kinetic processes more amenable to combustion control.[2]

2.1.3 Sulfuric Acid Mist and Sulfates

Sulfuric acid and sulfates are formed by oxidation of sulfur dioxide by several mechanisms, most involving reactive agents such as photochemical smog, ammonia, catalytic metals, and fine particulates. Temperatures and humidity also influence the reaction. Sulfuric acid can be found as a gas phase component or a condensed liquid aerosol, and it can also be adsorbed on carboneous particulate matter. In addition, free acid may react with metal oxides formed in the combustion flame to yield sulfates.[5] Sulfuric acid and its reaction products are primary sulfate emissions, contrasted with secondary sulfate derived from the transformation of SO_2 in the atmosphere.

Several factors influence the nature and extent of primary sulfate emissions. These include fuel characteristics, boiler design and operation, and emission controls. The extent of sulfate emissions can be affected by boiler design parameters, including the number and type of burners, residence time and temperature distribution, and the amount of internal surface area. Measurements have indicated that for a given fuel sulfur content, the total sulfate emissions from oil-fired sources are from 3 to 10 times greater than from sources burning coal and contain a large fraction of free sulfuric acid.[5]

Atmospheric sulfur dioxide may be oxidized to SO_3 and converted to sulfuric acid aerosol, or it may form sulfite ions that are then oxidized to sulfate. Subsequent to the oxidation, sulfuric acid or sulfate may interact with other materials to form other sulfate compounds. Sulfate formation rates are usually enhanced by increases in humidity. The mechanisms by which sulfur dioxide is oxidized to sulfates are not well understood but are important because they determine the formation rate and, to some extent, the final form of sulfate.[6] Most mechanisms involve reactive agents such as photochemical smog, ammonia, catalytic metals, and fine particulates. These agents can complicate the relationship between SO_2 and sulfates; for example, reductions or increases in SO_2 concentrations may not result in proportional reductions or increases in sulfate levels because of the other agents that affect the formation reaction.[7] Reduction in ambient sulfate concentration will result in a concommitant reduction in particulate matter concentration to the extent that sulfates are particulate matter.

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6. Ref. 1, pp. 22-24.

7. Ref. 1, p. x.

2.2 SULFUR OXIDES EMISSION TRENDS

Total SO_x emissions have been relatively stable over the first half of this decade. Ambient SO_x levels decreased in urban areas in the early 1970's, probably because of increasing use of fuels with lower sulfur content and a general shift of sulfur-emitting sources away from urban areas. After an initial improvement, the SO_x levels stabilized as the National Ambient Air Quality Standards were achieved in many areas. Since reaching a low in 1975, however, SO_x emissions have risen, as seen in Tables 2.2-1 (a and b).[1] The increases are due to greater fuel use and to the displacement of natural gas by oil and coal.

Sulfur oxides, primarily SO_2, are generated during combustion of any sulfur-bearing fuel and also in many industrial processes that use sulfur-bearing raw materials. Bituminous coal and residual fuel oil usually contain 1 to 3 percent sulfur by weight. Ordinary combustion of fossil fuels (at normal levels of excess air) forms SO_2 and SO_3 at a ratio of 30 to 1; when power plants are operated with controlled reaction conditions, the ratio of SO_2 to SO_3 is generally about 60 to 1.[2]

This section presents a summary of the 1976/1977 estimated SO_x emissions by sector and fuel type. It also presents an estimate of SO_x emission density for each county in the United States.

2.2.1 1977 SO_x Emissions

Table 2.2-2 presents the estimated SO_x emissions in 1977. These estimates are based on published data describing fuel use and industrial production and on other data from the Environmental Protection Agency (EPA) describing emission factors and emissions. The transportation category in Table 2.2-2 includes emissions from all mobile sources. Mobile sources include aircraft, trains, shipping, and miscellaneous sources. Stationary fuel combustion is defined as fuel used in nonmobile combustion equipment such as boilers and stationary internal combustion engines. Emissions are shown for electric utility power plants, industrial establishments, and other fuel consumers (residential, commercial, governmental, and educational). Industrial processes include emissions from the operation of process equipment by manufacturing industries. Solid waste includes emissions from

TABLE 2.2-1a. NATIONWIDE SO_X EMISSION TRENDS, 1970-1977[1]
(Tg/yr)

Source category	1970	1971	1972	1972	1972	1975	1976	1977
Transportation	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.8
Stationary fuel combustion	22.6	21.6	22.0	23.1	22.1	20.8	21.9	22.4
Industrial processes	6.3	5.8	6.7	6.3	5.6	4.6	4.5	4.2
Solid waste	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Miscellaneous	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0
	29.8	28.3	29.6	30.2	28.4	26.1	27.2	27.4

Note: A value of 0.0 indicates emission of less than 0.05 Tg/yr.

TABLE 2.2-1b. NATIONWIDE SO_X EMISSION TRENDS, 1970-1977[1]
(10^6 short tons/year)

Source category	1970	1971	1972	1973	1974	1975	1976	1977
Transportation	0.8	0.8	0.8	0.8	0.8	0.8	0.9	0.9
Stationary fuel combustion	24.9	23.8	24.3	25.5	24.4	22.9	24.1	24.7
Industrial processes	6.9	6.4	7.4	6.9	6.2	5.1	5.0	4.6
Solid waste	0.1	0.1	0.1	0.1	0.0	0.0	0.0	0.0
Miscellaneous	0.1	0.1	0.1	0.0	0.0	0.0	0.0	0.0
	32.8	31.2	32.0	33.3	30.7	28.8	30.0	30.2

Note: A value of 0.0 indicates emission of less than 55,000 short tons/yr.

TABLE 2.2-2. NATIONWIDE SO_X EMISSION ESTIMATES, 1977[1]

	Tg/yr	10^6 tons/yr
Transportation (total)	0.8	0.88
Highway vehicles	0.4	0.44
Nonhighway vehicles	0.4	0.44
Stationary fuel combustion (total)	22.4	24.69
Electric utilities	17.6	19.40
Industrial	3.2	3.53
Residential, commercial, and institutional	1.6	1.76
Industrial processes (total)	4.2	4.63
Chemicals	0.2	0.22
Petroleum refining	0.8	0.88
Metals	2.4	2.65
Mineral products	0.6	0.66
Oil and gas production and marketing	0.1	0.11
Industrial organic solvent use	0	0
Other processes	0.1	0.11
Solid waste	0	0
Miscellaneous	0	0
Forest wildfires	0	0
Agricultural burning	0	0
Coal refuse burning	0	0
Structural fires	0	0
Miscellaneous organic solvent use	0	0
Total	27.4	30.20

Zero indicates emissions of less than 0.05 Tg (55,000 tons) per year.

the combustion of waste in municipal and other incinerators and from the open burning of domestic and municipal refuse. Miscellaneous sources include emissions from the combustion of forest, agricultural, and coal refuse, and from structural fires.[3]

Table 2.2-3 presents the 1977 SO_x emissions from fuel combustion by sector and fuel type.

TABLE 2.2-3. SUMMARY OF 1977 SO_x EMISSIONS FROM FUEL COMBUSTION BY FUEL TYPE[4]

Sector	Percent by fuel type		
	Coal	Oil	Gas
Electric generation	68.5	7.7	<0.1
Industrial	7.6	6.1	0.6
Commercial/Institutional	0.5	3.7	<0.1
Residential	4.3	1.0	<0.1

As shown in Figure 2.2-1, 22.4 Tg (24.7 million tons) or approximately 82 percent of the national total was produced by fuel combustion in stationary sources. This category covers all fuel use in stationary combustion

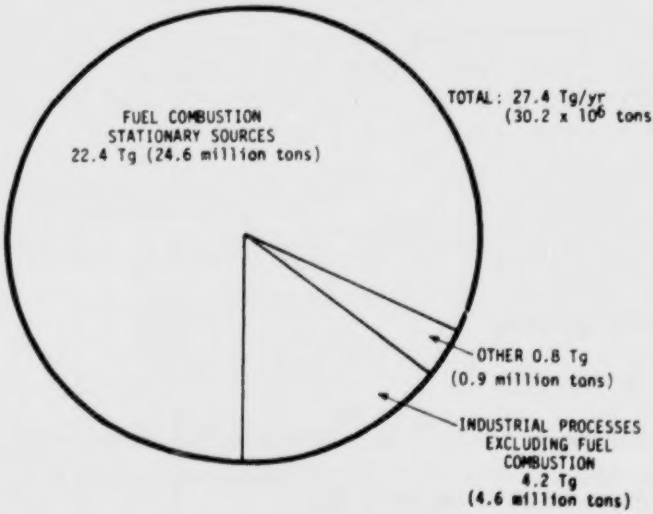

Figure 2.2-1. Nationwide sources of sulfur oxide emissions, 1977.[1]

equipment such as boilers and stationary internal combustion engines; it encompasses electric utility power plants, industrial establishments, and other fuel consumers (residential, commercial, governmental, and institutional). Industrial processes generated an additional 4.2 Tg (4.6 million tons). The remainder, 0.8 Tg (0.9 million ton), was emitted by miscellaneous sources such as burning coal refuse banks, agricultural burning, combustion of fuels for transportation, and disposal of solid wastes. It should be noted that sulfur oxide emissions by source in any given locality may differ markedly from those in Figure 2.2-1.

2.2.2 Emission Density of SO_x Emissions in the United States

This section describes the geographical variation in emission density across the continental United States. Figure 2.2-2 is a map of the United States with each county shaded according to its estimated SO_x emission density. These data represent the emission density at the midpoint of the decade, the base year being 1975. The highest SO_x emission densities are found in the Northeast, where there is heavy usage of fossil fuels containing sulfur compounds, and in several isolated counties in the West, where many smelters are located. Approximately 26 percent of the total U.S. population live in areas with SO_x emission densities exceeding 35 megagrams per square kilometer (100 tons per square mile). Over half of the population live in areas with emission density greater than 3.5 megagrams per square kilometer (10 tons per square mile); these areas represent 11 percent of the land area of the continental United States.[5]

2.2.3 Trends in SO_x Emissions

Figure 2.2-3 represents the estimated SO_x emissions from 1970 to 1977. During this period the emissions decreased slightly. Emissions from electric utilities actually increased by 10 percent during this period. This increase would have been substantially higher had it not been for the use of fuels with lower sulfur content, because the amounts of coal and residual oil burned during this period increased about 50 percent and 70 percent respectively. Emissions of SO_x from industrial processes were significantly

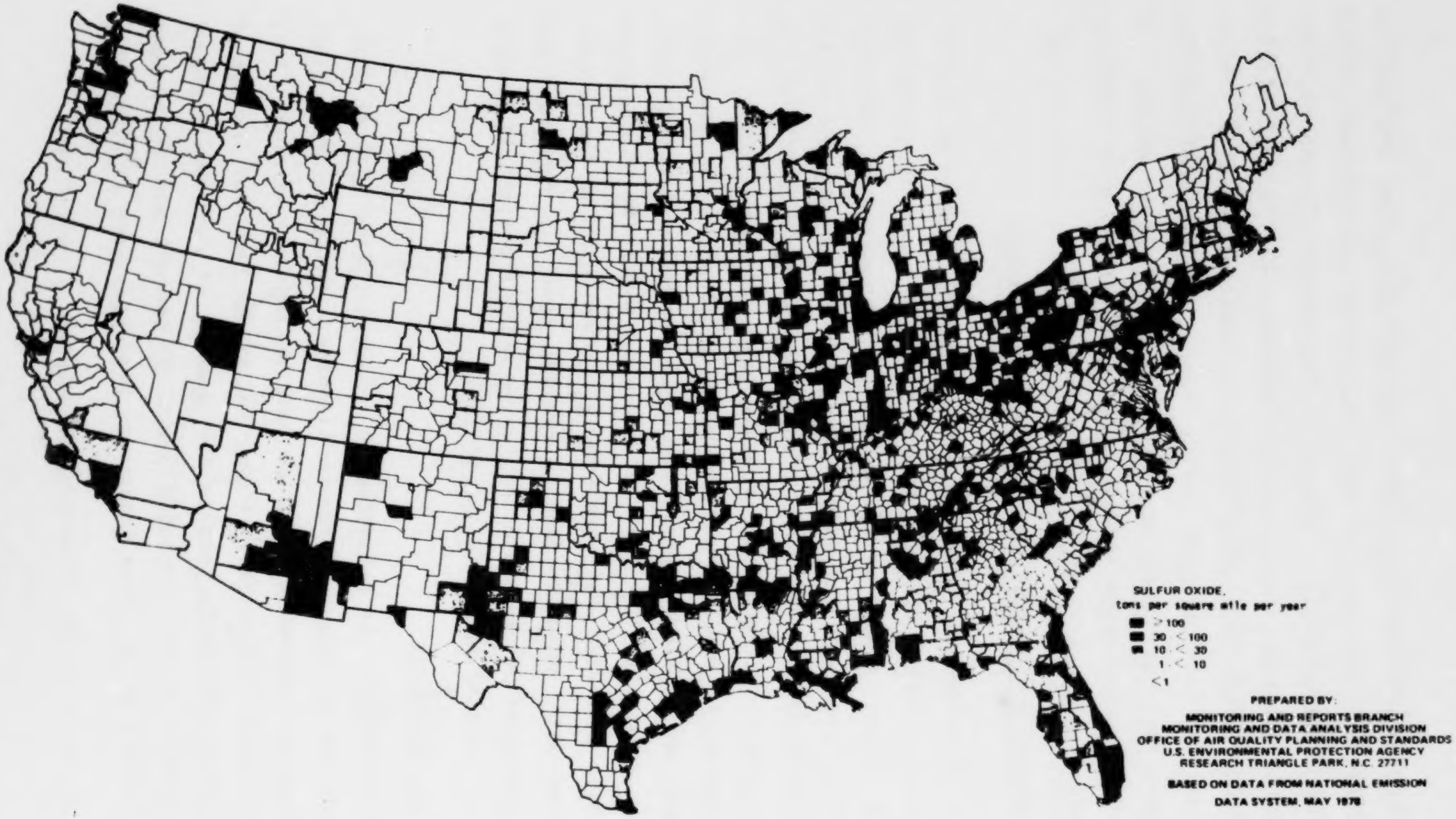
SULFUR OXIDE,
tons per square mile per year
>100
30 < 100
10 < 30
1 < 10
<1
PREPARED BY:
MONITORING AND REPORTS BRANCH
MONITORING AND DATA ANALYSIS DIVISION
OFFICE OF AIR QUALITY PLANNING AND STANDARDS
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, N.C. 27711
BASED ON DATA FROM NATIONAL EMISSION
DATA SYSTEM, MAY 1978

Figure 2.2-2. Significant areas of sulfur oxide emission.[5]

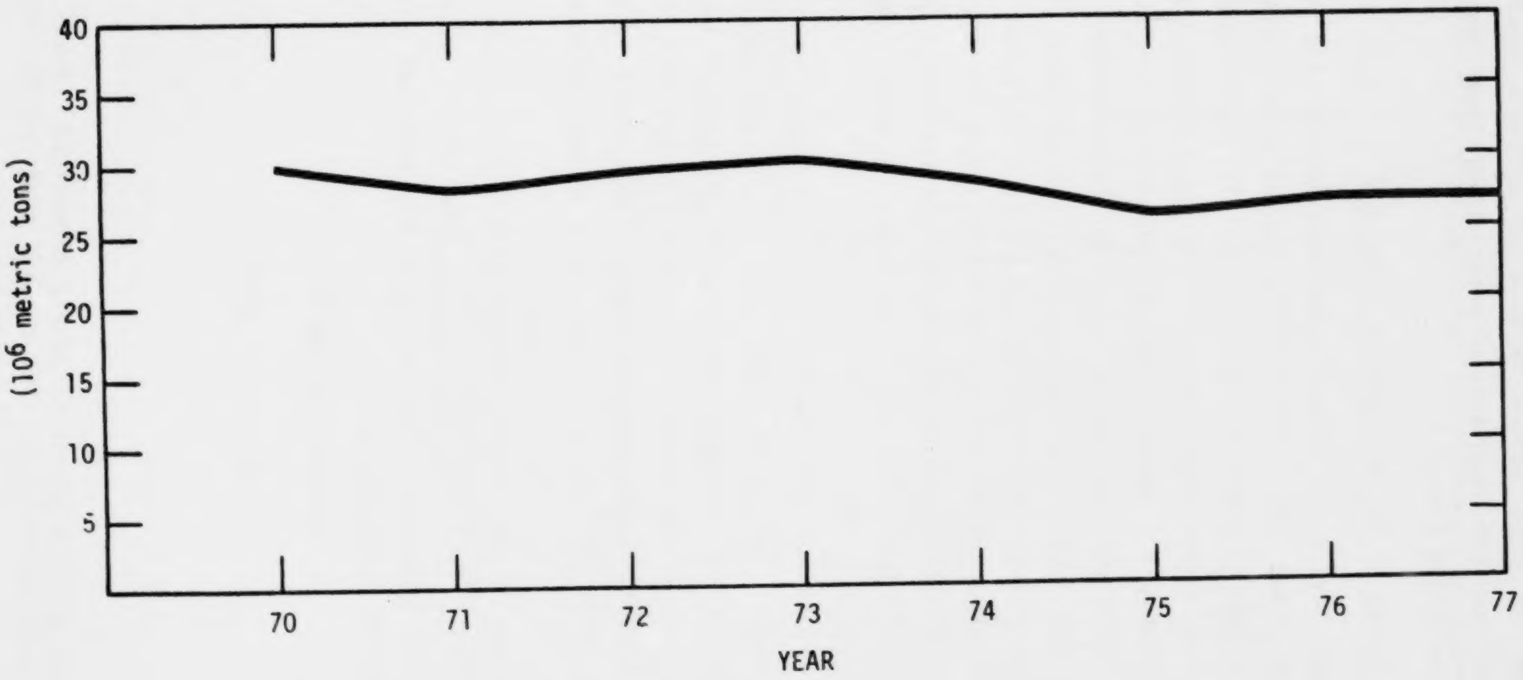

Figure 2.2-3. Nationwide SO_x emission trends 1970-1977.[1]

lower in 1977 than in 1970, mainly because of controls used by primary nonferrous smelters and EPA regulations prescribing lower emissions from sulfuric acid manufacturing plants.[6]

2.2.4 Nationwide Trends in SO_x Air Quality 1970-1977

Sulfur dioxide levels in urban areas throughout the Nation have gradually decreased since 1970. The 1972-77 trends show dramatic initial improvement (see Figure 2.2-4) followed by fairly consistent continuing improvement. In most urban areas, this is consistent with the switch in emphasis from attainment of standards to maintenance of air quality; that is, the initial effort was to reduce pollution to acceptable levels and subsequent efforts have been to maintain air quality at these lower levels.

Sites providing data for these analyses were selected from EPA's National Aerometric Data Bank. Sites for assessment of trends in the 1972-1977 time period were selected to ensure the historical completeness and seasonal balance of data. For SO_2, 1233 sites recorded sufficient data to qualify as trend sites.

Figure 2.2-4 illustrates nationwide trends in annual mean SO_2 levels from 1972 through 1977. The graph shows that SO_2 levels continued to improve in the middle 1970's although the rate of improvement was much less pronounced than earlier in the decade. From 1972 through 1977, the national average SO_2 level dropped 17 percent, an annual improvement rate of 4 percent per year. As would be expected, most sites showed improvement during this period.

Short-term changes in SO_2 levels between 1976 and 1977 were mixed, with no predominant trends. Most SO_2 monitors in urban areas reported levels well below the annual standard. The remaining SO_2 problems are primarily associated with specific point sources.[7]

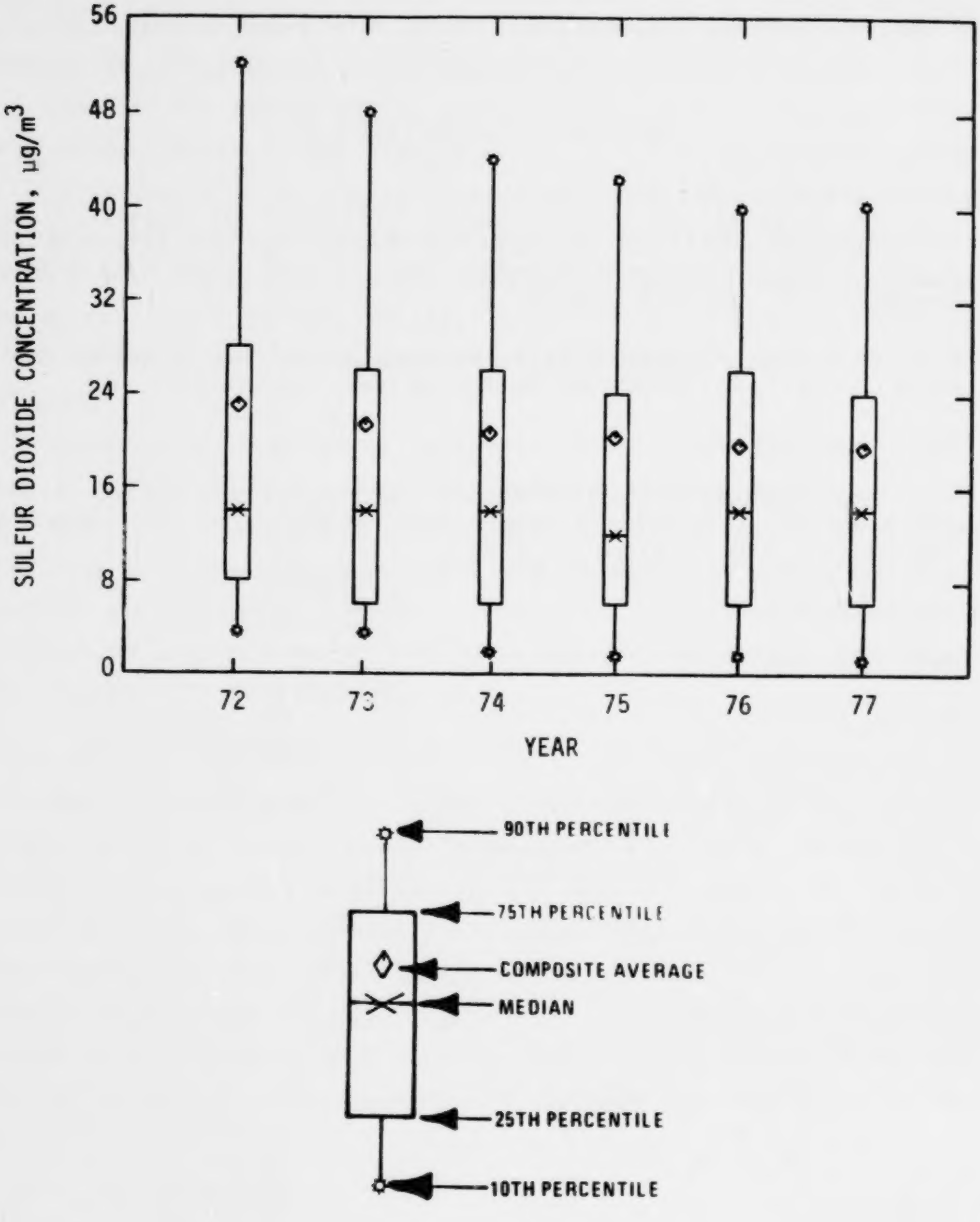

Figure 2.2-4. Nationwide trends in annual average sulfur dioxide concentrations from 1972 to 1977 at 1,233 sampling sites.[8]

REFERENCES FOR SECTION 2.2

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2.3 SAMPLING AND ANALYSIS METHODS

This section deals with manual and automated methods for sampling and analysis of sulfur oxides in ambient air and at emission sources.

Ambient air monitoring is conducted for several reasons. Some state regulations require that industries monitor the atmosphere for certain pollutants specific to their source, and some states permit ambient air monitoring in lieu of compliance with a specified emission limitation. Ambient monitoring also provides information that is useful in determining the normal levels of air quality, in following air quality trends, and in providing guidance for emergency control procedures during air pollution episodes.

Measurement of pollutant emissions in the stack of an industrial process is referred to as stack gas sampling, source testing, or emissions testing. Such measurements may be used to determine whether a source is complying with emission regulations and to determine the efficiency of an emission control device. Where a process design must be altered to correct a pollution problem, source test data may provide a basis for determining what changes will be most effective.

2.3.1 Ambient Monitoring

Ambient monitoring for oxides of sulfur, primarily SO_2, may be performed by using either manual methods or continuous analyzers. Manual methods involve operators collecting and analyzing samples at various steps of the analysis; these methods yield values that are integrated over specified sampling periods. Even though many steps in the analysis may be automated, the procedure is still considered a manual method. In continuous SO_2 monitoring all sampling and analysis are performed without direct involvement by an operator; the measurements are made continuously on a real-time basis.

2.3.1.1 Manual Methods--

The EPA has designated the manual pararosaniline method as its reference method for analysis of SO_2 in ambient air.[1] This colorimetric procedure, developed by West and Gaeke in 1956,[2] utilizes gas bubblers as the SO_2 collection system. Basically, the SO_2 is scrubbed into a potassium tetrachloromercurate (TCM) solution to form a stable dichlorosulfitomercurate complex, which then undergoes reaction with pararosaniline and formaldehyde to form the colored complex of pararosaniline methylsulfonic acid. The colored complex is measured colorimetrically to determine the SO_2 value.

These values are reported as an average number of micrograms of SO_2 per cubic meter of air passing through the bubbler during the sampling period, which is normally 24 hours.

2.3.1.2 Continuous Monitoring--

Automated methods for continuous ambient monitoring of sulfur oxides must be EPA reference or equivalent methods. The definition and qualifications of reference and equivalent methods are given in Federal regulations (40 CFR 53). Table 2.3-1 lists the analyzers that have been designated as equivalent methods in accordance with 40 CFR 53. Each of these analyzers must be used in strict accordance with the operation or instruction manual.*

The Lear Siegler Model SM 1000 SO_2 Ambient Monitor is based on second-derivative spectroscopy. The narrow-band absorption of electromagnetic radiation exhibited by SO_2 in the ultraviolet region produces an output signal that is processed to give SO_2 concentration readings. A second-derivative spectrometer processes the transmission-versus-wavelength function of an ordinary spectrometer to produce an output signal proportional to the second derivative of this function. This technique enhances the sensitivity of an ordinary spectrometer. The SM 1000 SO_2 Ambient Monitor has been developed specifically to measure SO_2 gas concentrations in parts per billion.

Both the Meloy Model SA185-2A Sulfur Dioxide Analyzer and the Monitor Labs Model 8450 Sulfur Monitor use flame photometry, in which a hydrogen flame excites the SO_2 molecules and causes the emission of light. A narrow-band filter selects the light emitted at 394 nanometers (nm), which

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* A current list of analyzers designated as reference or equivalent methods for SO_2 is available from the U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Dept. E, MD-76, Research Triangle Park, North Carolina 27711.

TABLE 2.3-1. AUTOMATED EQUIVALENT METHODS FOR AMBIENT SULFUR DIOXIDE MONITORING[a]

Equivalent analyzer	Principle of operation
Lear Siegler Model SM 1000 SO_2 Ambient Monitor	Second derivative Ultraviolet absorption
Meloy Model SA 185-2A Sulfur Dioxide Analyzer	Flame photometry
Monitor Labs Model 8450 Sulfur Monitor	Flame photometry
Thermo Electron Model 43 Pulsed Fluorescent SO_2 Analyzer	Fluorescence spectrometry
Beckman Model 953 Fluorescent Ambient SO_2 Analyzer	Fluorescence spectrometry
Philips PW 9700 SO_2 Analyzer	Coulometric
Philips PW 9755 SO_2 Analyzer	Coulometric
ASARCO Model 500 Sulfur Dioxide Monitor	Conductimetric
Bendix Model 8303 Sulfur Analyzer	Flame photometry
Meloy Model SA 285-E Sulfur Dioxide Analyzer	Flame photometry

[a] Listing issued by Environmental Monitoring and Support Laboratory, EPA. February 22, 1979

is then detected by a photomultiplier tube. The resultant photomultiplier signals are amplified and processed to give readings of SO_2 concentration.

The Thermo Electron Model 43 Pulsed Fluorescent SO_2 Analyzer and the Beckman Model 953 Fluorescent Ambient SO_2 Analyzer use fluorescence spectrometry. Fluorescence is defined as the emission of light absorbed by a molecule; the emitted light is of a different wavelength from that of the absorbed light. In the fluorescence technique the SO_2 molecule is irradiated with light at a given wavelength (usually in the near-ultraviolet region), and the emitted light is measured at a longer wavelength. The resultant fluoresence, directly proportional to the number of SO_2 molecules present, is then measured by a photomultiplier tube. The photomultiplier signals are amplified and processed to give readings of SO_2 concentrations. The commercially available instruments contain either a continuous light source (used in the Beckman model) or a pulsed ultraviolet light source (used in the Thermo Electron Model).

The Philips PW 9755 and PW 9700 SO_2 Analyzers operate on the coulometric principle. The analyzer measures the current generated in an electrochemical reaction such as

$$2Br \rightarrow Br_2 + 2e^- .$$

Sulfur dioxide affects this reaction in the following manner:

$$SO_2 + 2H_2O + Br_2 \rightarrow H_2SO_4 + 2HBr.$$

The instrument measures the change of current flow due to the change in the rate of Br_2 generation caused by the presence of SO_2. The change in current is processed to give readings of SO_2 concentration.

The ASARCO Model 500 Sulfur Dioxide Monitor senses the change in electrical conductivity in water when a soluble substance such as SO_2 is dissolved in it. The change of conductivity is proportional to the concentration of SO_2 added and is easily measured to give SO_2 concentration readings.

2.3.2 Source Monitoring

Source monitoring for oxides of sulfur may be performed by using manual methods or automated continuous analyzers. Manual methods that may be used are EPA Method 6 and EPA Method 8. EPA Methods 6 and 8 are used as the manual reference methods for determination of compliance with NSPS. Automated continuous analyzers are usually used as indicators of continued complying operation. Two exceptions are the primary lead and electric utility NSPS, where the instrumental method is required to generate compliance data. Automated continuous analyzers fall into two main classes: extractive and in-situ systems. Remote monitoring systems have been developed, but they will not be discussed because they are mainly experimental and still in the development stage.

2.3.2.1 Manual Methods--

The EPA Method 6 is the required reference method for determining emissions of SO_2 from stationary sources (except sulfuric acid plants) subject to New Source Performance Standards.[3] Many states have adopted Method 6 for all stationary sources. Both Methods 6 and 8 (discussed later) are valid for any source emitting SO_2 and/or sulfuric acid mist.

In sampling for SO_2 using Method 6, a gas sample is taken at a single sampling point located at the center of the stack or no closer to the wall than 1 meter (3.28 feet). The sample must be extracted at a constant rate.

The collected gases are bubbled through solutions contained in impingers, which trap sulfur oxides in a soluble and stable form for subsequent analysis. As the gas goes through the sampling apparatus, the sulfuric acid mist and SO_3 are removed in the first impinger containing 80 percent isopropyl alcohol, the SO_2 is removed by a chemical reaction with a 3 percent hydrogen peroxide solution contained in the two subsequent impingers, and the sample gas volume is measured. The sulfuric acid mist and SO_3 are discarded, and the collected material containing the SO_2 is recovered for laboratory analysis. The concentration of SO_2 in the sample is determined by titrating the sample with barium perchlorate in the presence of the indicator thorin.

Method 6 requires a sampling time of 20 minutes per sample, and two separate samples constitute a run. The method specifies three runs, resulting in six separate samples. The method can determine stack concentrations of 50 to 10,000 ppm of SO_2.

The EPA Method 8 is the reference method for determining emissions of sulfuric acid mist (including SO_3) and SO_2 from sulfuric acid plants.[4] The collection system utilizes an 80 percent isopropyl alcohol solution in the first impinger and hydrogen peroxide in the two subsequent impingers. The impingers are similar to those in Method 6, but in Method 8 the isopropyl alcohol water solution that traps the sulfuric acid mist and SO_3 is also titrated with barium perchlorate to determine the sulfuric acid and SO_3 concentrations.

2.3.2.2 Continuous Methods--

Continuous emissions analysis consists of extractive and in-situ monitoring systems. Extractive systems consist of removing a continuous sample from the gas stream, conditioning the sample (removal of particulate and excess water vapor), and transporting the sample stream to a remotely located analyzer for analysis. Remote signifies only that the analyzer is located outside the duct. Actual distance may be as little as 3m (10 ft) or greater than 100 m (300 ft).

In-situ systems analyze the gas as it exists in the stack or duct, generally by some advanced spectroscopic technique. The analyzers are installed across a stack (cross-stack) or employ a sensor inserted into the flue gas stream (in-stack). Both extractive and in-situ monitoring systems used for source emissions measurements must meet EPA performance specifications at the time of installation and throughout their operation. A summary of the current specifications is presented in Table 2.3-2.

Continuous methods using extractive systems--The extractive instruments in use today for SO_x monitoring utilize nondispersive infrared or ultraviolet techniques, fluorescence, flame photometry, and electrochemical methods.

Nondispersive infrared and ultraviolet techniques are based on light absorption spectroscopy. Light is passed through a gas, and the degree of absorption of certain infrared or ultraviolet wavelengths is measured. For SO_2, the sensitivity of nondispersive infrared (NDIR) instruments is usually about 10 ppm. The sampling system used in tandem with an NDIR analyzer

TABLE 2.3-2. CURRENT PERFORMANCE SPECIFICATIONS FOR CONTINUOUS MONITORING SYSTEM AND EQUIPMENT[5]

Parameter	Specification
Accuracy[a]	$\geq$ 20 percent of the mean value of the reference method test data
Calibration error[a]	$\geq$ 5 percent of each (50 percent, 90 percent) calibration gas mixture value
Zero drift (2-hour)[a]	2 percent of span
Zero drift (24-hour)[a]	2 percent of span
Calibration drift (2-hour)[a]	2 percent of span
Calibration drift (24-hour)[a]	2.5 percent of span
Response time	15 minutes maximum
Operational period	168 hours minimum

[a] Expressed as sum of absolute mean value plus 95 percent confidence interval of a series of tests.

contains filters that remove particulates, sulfuric acid mist, and water from the flue gas stream. Nondispersive ultraviolet (NDUV) analyzers, sometimes called differential absorption analyzers, are more sensitive and are not subject to the same interferences (e.g., H_2O, CO_2). They are, however, heavy and bulky. Some manufacturers of NDUV monitors are DuPont, CEA Instruments, Esterline-Angus, and Teledyne.

Fluorescence techniques are based on emission spectroscopy. Molecules or atoms are energized by exposure to high-intensity ultraviolet radiation; they emit light at specific wavelengths, and the amount of emitted light is measured.

Ultraviolet fluorescence methods are used for analysis of SO_2 both in ambient air and at stationary sources. Celesco Industries, Inc., manufactures a fluorescence instrument with a continuously emitting UV light source, whereas a unit made by Thermo Electron Corporation utilizes a pulsed light source.

Flame photometry is another luminescence technique used to detect SO_2. Instead of exciting the SO_2 molecules with an ultraviolet light source as in fluorescence methods, flame photometry uses a hydrogen flame. The resulting emitted light is measured and recorded as an SO_2 concentration. Flame photometric analyzers are used primarily in ambient monitoring, but are applied to stationary source monitoring by use of sample dilution systems. Tracor, Melory Laboratories, Bendix Corp., Process Analyzers, and others manufacture flame photometric analyzers.

Three classes of analyzers work on electrochemical principles: conductimetric, coulometric, and polarographic (the electrochemical cell). The conductimetric (electrical conductivity) principle was briefly discussed earlier. Calibrated Instruments, Inc., (Mikrogas-MSK) produces a conductimetric analyzer that absorbs SO_2 in a hydrogen peroxide solution. Manufacturers of coulometric analyzers include Barton ITT and Beckman Instruments, Inc. The coulometric analyzer can be operated unattended for extended periods of time.

Polarographic analyzers measure the current induced by electrochemical oxidation of SO_2 at a sensing electrode. Dynasciences, Beckman Instruments, Inc., Theta Sensors, and Teledyne market polarographic analyzers.

Automated methods using in-situ systems--In-situ, cross-stack, or in-stack monitors use electro-optical techniques based on infrared or ultraviolet absorption. The four most common electro-optical principles used in these instruments are 1) dispersive spectroscopy, 2) gas-filter correlation spectroscopy, 3) dispersive correlation spectroscopy, and 4) second-derivative spectroscopy.

A dispersive absorption spectrometer can be set at any wavelength within its range; in this it differs from a nondispersive instrument, which looks at a broad spectral region and must be sensitized to detect each particular gas by means of a detector cell. Environmental Data Corporation currently markets an on-stack monitor utilizing this technique. Wilks Scientific Corporation produces a series of portable dispersive infrared analyzers that are applicable to stack gas monitoring and to analysis of process streams and in-plant air.

A gas-filter correlation spectrometer discriminates between gases by correlating the structure of the spectrum of the gas species to be measured in the stack with the spectrum of the same species contained in a correlation cell (gas cell). Correlation spectrometers have demonstrated potential for stationary source monitoring. Environmental Research and Technology manufactures an instrument that measures SO_2 by this technique.

Dispersive correlation spectroscopy combines the techniques of gas-filtered correlation and dispersive in-situ monitors. Barringer Research, Ltd., of Canada is actively developing correlation spectrometers and offers units commercially for SO_2 source monitoring.

Second-derivative spectroscopy, discussed earlier, has only recently been applied to the measurement of air pollutants. Lear-Siegler, Inc., markets a series of spectrometers based on this principle for SO_2 monitoring.

Although in-situ monitors are relatively new, they are meeting performance specifications and offer certain operational advantages for facilities required to monitor source emissions continuously.

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4. U.S. Environmental Protection Agency. Reference Method 8 - Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources. 40 CFR 60, Appendix A. July 1980.

5. U.S. Environmental Protection Agency. Performance Specifications. 40 CFR 60, Appendix B. July 1980.

SECTION 3

CONSIDERATIONS IN SULFUR OXIDES CONTROL

This section presents a general outline of items that should be evaluated for sulfur oxide emission sources.

The first subsection presents information on energy availability and usage trends in which energy policy is reviewed. The second subsection discusses the determination of the emission reduction needs and includes information on State Implementation Plans (SIP), New Source Performance Standards (NSPS), Prevention of Significant Deterioration, and visibility regulations, as well as an introduction to dispersion modeling. The third subsection presents an outline of technical considerations in sulfur oxide control. The fourth subsection discusses environmental and energy impacts and technical considerations. The fifth subsection reviews the market for sulfur and sulfur-related products that may be recovered and offered for sale as products of some sulfur oxide emission reduction systems.

3.1 ENERGY AVAILABILITY AND USAGE TRENDS

The 1970's have brought soaring energy prices and the prospect of future energy shortage. The oil embargo of 1973-74 pointed up an enormous and growing energy demand, with which domestic fuel production has not kept pace. As a result, alternative energy technologies are being sought to reduce the dependence on energy from other sources. Short-term strategies are being developed; their overall effect is intended to be a return to a far greater dependence on fuels with proven domestic reserves, such as coal.

A move toward increasing use of coal brings special problems for industry. An increase in the use of coal for energy independence would necessitate the installation of pollution control equipment, not only for cleaning the stack gas, but also for acceptable disposal of the tons of bottom ash and fly ash generated in the firing of coal.

Combatting an energy shortage in an energy-intensive nation is a difficult problem. This section discusses some of the methods proposed to date for coping with the situation.

3.1.1 U.S. Energy Policy

The availability and future usage of fuels in the United States is being greatly influenced by a series of national acts aimed at stemming the use of imported crude oil and natural gas. Reserves of petroleum have been located in Alaska, but even they are insufficient to reduce the dependence upon Middle East oil. As a result, several short-term plans have been enacted to curb the rate of increase of petroleum fuel usage.

3.1.1.1 The Energy Supply and Environmental Coordination Act (ESECA) of 1974 (PL 93-319) as Amended by the Energy Policy and Conservation Act (EPCA) (PL 94-163)--

As a direct consequence of the 1973 oil embargo, Congress passed ESECA to institute a reduction of oil and natural gas usage by major combustors in the United States. The purpose of the Act, as it relates to fuel usage, is stated in a pamphlet issued by the Federal Energy Administration (FEA): "ESECA is based upon expanding the use of U.S. reserves of coal, considering the environmental consequences of that use, and recognizing that in some cases, previous environmental requirements may unnecessarily preclude the use of coal."[1] Knowing that the National Environmental Policy Act of 1969 would require extensive investigation regarding the effects of fuel changes on air and water quality, Congress required close coordination and cooperation between the EPA and the FEA. The authority granted to the FEA under ESECA consisted of the following:[2]

The FEA could--

- Prohibit a power plant or major fuel burning installation (MFBI) from burning petroleum or natural gas under certain defined conditions,
- Order power plants and MFBI's in the "early planning process" to be constructed and designed for coal firing as their primary energy source, and
- Allocate coal supplies, if necessary, to implement their prohibition orders.

The EPA was included in the Act as a participant in the prohibition process to ensure that the State Implementation Plan would be met assuming total coal firing in a converted unit.

The authority of ESECA expired on June 30, 1977. During the 1974 through 1977 period, many plants were evaluated for their coal-firing capabilities. Because of such factors as age, availability of fuel, size of the unit, and environmental constraints, only a few plants were issued final prohibition orders. A total of 58 coal conversion orders were issued as of June 30, 1977, when the Act expired.[3]

In the Congress at that time were the rudiments of a new comprehensive energy bill intended to supersede the ESECA authority and change the overall context of the prohibition order process. The cabinet-level Department of Energy was established in late 1977.

The Congress passed the National Energy Act on October 15, 1978. The Act is composed of five parts:

- The National Energy Conservation Policy Act of 1978,
- The Power Plant and Industrial Fuel Use Act of 1978,
- The Public Utilities Regulation Policy Act,
- The Natural Gas Policy Act of 1978, and
- The Energy Tax Act of 1978.

Although each of these acts has some indirect effect on the availability and usage of fuels, it is the Power Plant and Industrial Fuel Use Act (FUA) that carries on the ESECA coal-firing strategies. Further prohibition of petroleum and natural gas usage under FUA will have the most direct impact on the availability and utilization of the various fuel types in the industrial and utility sectors.

3.1.1.2 The Fuel Use Act of 1978--

The Power Plant and Industrial Fuel Use Act of 1978, as quoted below, has several provisions:[4]

> Prohibition of New Oil and Gas-Fired Boilers
>
> Prohibition against use of oil or natural gas in new electric utility generation facilities or in new industrial boilers rated at 29.3 MW (thermal) (with a fuel heat input rate of 100 million Btu's per hour or greater), unless exemptions are granted by DOE.
>
> Restrictions on Existing Coal Capable Large Boilers
>
> DOE authority to require existing coal capable facilities, individually or by categories, to use coal and to require noncoal capable units to use coal-oil mixtures.
>
> Restrictions on Users of Natural Gas for Boiler Fuel
>
> Limitation of natural gas use by existing utility power plants to the proportion of total fuel used during 1974-1976, and a requirement that there be no switches from oil to gas. There is also a requirement that natural gas use in such facilities cease by 1990 with certain exceptions. [If a power plant began operation on or after January 1, 1974, the use of natural gas is limited to the average quantity of gas used during the first 2 years of operation. Any new facility must be designed to be coal-capable.]
>
> Pollution Control Loan Program
>
> An $800 million loan program to assist utilities to raise necessary funds for pollution control.
>
> Supplemental Authority
>
> Supplemental authority to prohibit use of natural gas in small boilers for space heating and in decorative outdoor lighting and to allocate coal in emergencies.
>
> Other Provisions
>
> Funding of several programs to reduce negative impacts from increased coal production; energy impact assistance and railroad rehabilitation.

A significant modification in the prohibition order process is that the owner of an existing power plant or MFBI (or one that is proposed for construction) must petition the DOE, stating the reasons for being exempted from the oil prohibition. The petition is evaluated by the DOE's Economic Regulatory Administration (ERA), which then issues a Fuels Decision Report. This process requires considerable time and effort. It places the burden on the petitioner rather than the United States Government. The DOE has issued "interim final" rules for implementing the FUA. The final rules are to be issued. A petitioner may be granted a temporary or permanent exemption from coal firing for:

- Excessive cost burden. This exemption may be granted if the cost of burning coal is 30 to 50 percent greater than the cost of firing imported crude oil.
- Future use of innovative technologies (such as fluidized-bed combustion).
- Environmental constraints.
- Public interest criteria.
- Alternative fuels. A list of about 16 alternative fuels exists, other than oil or natural gas cogeneration.
- Fuel mixtures. A fuel containing at least 25 percent oil or natural gas may be considered.
- Site limitation.
- Future use of synthetic fuel. Exemption may be granted for a period pending development of the fuel.
- Capital availability.
- Product or process requirement.
- Numerous peak, reliability, and intermediate-load exemptions for utility units.

3.1.2 Current Availability and Usage

The overall policy has not yet significantly altered the distribution of fuels in use in the United States, however, as evidenced by Department of Commerce data.

The U.S. Department of Commerce, Bureau of the Census, compiles an "Annual Survey of Manufacturers,"[5] which presents information on the consumption of fuels and electric energy The survey issued in March 1978 is a three-volume report presenting energy usage by all manufacturing industries in 1976.[6] The results of this study are summarized in Table 3.1-1. Both consumption and cost of fuel have risen.

The relative distribution of fuel usage is presented in Table 3.1-2, which shows the fuel trends for selected years since 1962.[6] Although the 1977 survey is not yet available, it is anticipated that the use of coal will have increased slightly with decreasing oil usage. Table 3.1-2 shows the decrease in natural gas usage; even with the recent release of gas allotments to industry, it is expected that natural gas usage cannot increase for a prolonged period.

Costs of fuel, expressed in dollars per kilojoule (and dollars per million Btu) have been tabulated and indexed by the Department of Commerce. A composite cost chart is shown in Figure 3.1-1.[7] The year 1971 is selected to represent an index value of 100. The costs of all fuels have increased sharply since 1971. The cost of natural gas increased nearly 40 percent between 1974 and 1976. The relative cost of electricity as fuel has always been high, since it is a secondary fuel.

In spite of the shortage of domestic crude oil, the Bureau of the Census data show no indication of any radical curtailments due to the unavailability of any fuel. No forced shutdowns of production or other critical actions of any magnitude have been taken. It appears then, that the energy supplies required by the industrial and utility sectors are available under current conditions. It is generally believed, however, that the economic domination imposed by the Organization of Petroleum Exporting Countries (OPEC) will tighten the reins on oil supplies and cause continual increases in energy cost. As a result, domestic users will be obliged to switch to fuel types in reserve in the short term, and we must undertake concurrent research and development of future (long-term) technologies to meet an increasing energy demand.

TABLE 3.1-1. QUANTITY AND COST OF PURCHASED FUELS AND ELECTRIC ENERGY USED FOR HEAT AND POWER: 1976 AND SELECTED EARLIER YEARS BY MANUFACTURING INDUSTRIES[6]

	1958	1962	1967	1971	1974	1975[a]	1976
Purchased fuels and electric energy,							
kWh x 10^{12}	2.415	2.873	3.458	3.807	3.956	3.527	3.697
Btu x 10^{12}	8,247.8	9,810.5	11,810.3	13,002.3	13,509.8	12,044.4	12,625.3
Total cost, \$ x 10^6	5,067.0	6,184.1	7,691.7	10,432.1	19,433.4	23,237.2	27,586.9
Purchased fuels,							
kWh x 10^{12}	2.162	2.559	3.031	3.329	3.345	2.936	3.062
Btu x 10^{12}	7,384.9	8,739.2	10,351.7	11,370.2	11,424.8	10,026.7	10,458.9
Total cost, \$ x 10^6	2,836.2	3,360.7	3,974.9	5,360.6	10,983.9	12,951.1	15,505.1
Fuel oil,							
Residual,							
10^6 m^3	b	23.99	17.96	22.37	27.20	28.21	36.51
10^3 barrels	b	150,885.0	112,958.9	140,726.4	171,095.3	177,452.4	229,614.6
Cost, \$ x 10^6	b	432.4	298.7	535.9	1,964.9	2,149.0	2,718.2
Distillate,							
10^6 m^3	26.44[b]	1.111	10.44	16.68	18.10	16.68	14.92
10^3 barrels	166,301.0[b]	44,730.0	65,653.9	104,940.8	113,823.6	104,894.2	93,838.1
Cost, \$ x 10^6	522.7[b]	190.9	236.9	453.4	1,350.4	1,369.7	1,292.5
Bituminous coal, lignite, and anthracite,							
Tg	74.19	81.14	68.13	55.69	43.37	40.48	43.38
10^3 short tons	81,784.0	89,438.0	75,100.0	61,392.6	47,806.8	44,623.3	47,817.1
Cost, \$ x 10^6	638.2	639.5	551.7	658.1	1,083.1	1,310.3	1,341.6
Coke and breeze							
Tg	12.32	16.10	12.30	12.47	13.80	11.94	14.21
10^3 short tons	13,585.0	17,747.0	13,562.5	13,742.8	15,215.2	13,156.8	15,665.7
Cost, \$ x 10^6	271.0	304.8	248.9	317.6	744.6	880.8	1,141.2
Natural gas[c]							
10^9 m^3	88.14	122.0	150.3	182.8	186.0	164.4	167.2
10^9 ft^3	3,112.2	4,308.1	5,306.9	6,454.4	6,566.4	5,804.8	5,902.7
Cost, \$ x 10^6	900.9	1,455.9	1,749.1	2,559.9	4,360.1	5,653.1	7,535.5
Other fuels[d] \$ x 10^6	147.9	337.1	220.2	377.5	702.6	849.5	906.7
Fuels not specified by kind \$ x 10^6	355.6	0.0	669.4	458.2	778.1	738.7	569.2
Electric energy,							
Purchased,							
10^6 kWh	252,909.0	313,961.0	427,465.1	514,612.7	611,094.5	591,342.5	634,934.6
Cost, \$ x 10^6	2,230.8	2,823.3	3,716.8	5,070.6	8,449.4	10,286.3	12,081.9
Generated less sold							
10^6 kWh	66,850.0	74,261.0	78,355.8	82,828.0	80,932.3	63,275.0	64,571.1

[a] Revised.

[b] For 1958, figures are combined for residual and distillate.

[c] For 1967 and earlier; includes manufactured, still, blast-furnace, and coke-oven gas.

[d] For 1971 and later; includes gas (except natural).

TABLE 3.1-2. PERCENT OF TOTAL ENERGY CONSUMED FOR SELECTED INDIVIDUAL FUELS AND PURCHASED ELECTRICITY, BY MANUFACTURERS[6]

Fuel or electricity item	1976[a]	1975[a]	1974[a]	1971[a]	1967[a]	1962
TOTAL	100	100	100	100	100	100
Residual fuel oil	12	10	9	7	7	10
Bituminous coal, lignite, and anthracite	10	10	10	13	19	24
Coke and breeze	3	3	3	3	3	5
Distillate fuel oil	4	5	5	5	4	3
Natural gas	49	52	54	56	54	45
Purchased electricity	17	17	16	13	12	11
Other fuels	4	4	3	2	1	2

[a] Data for fuels not specified by kind are distributed among detailed fuels. Entries may not add to 100 because of independent rounding.

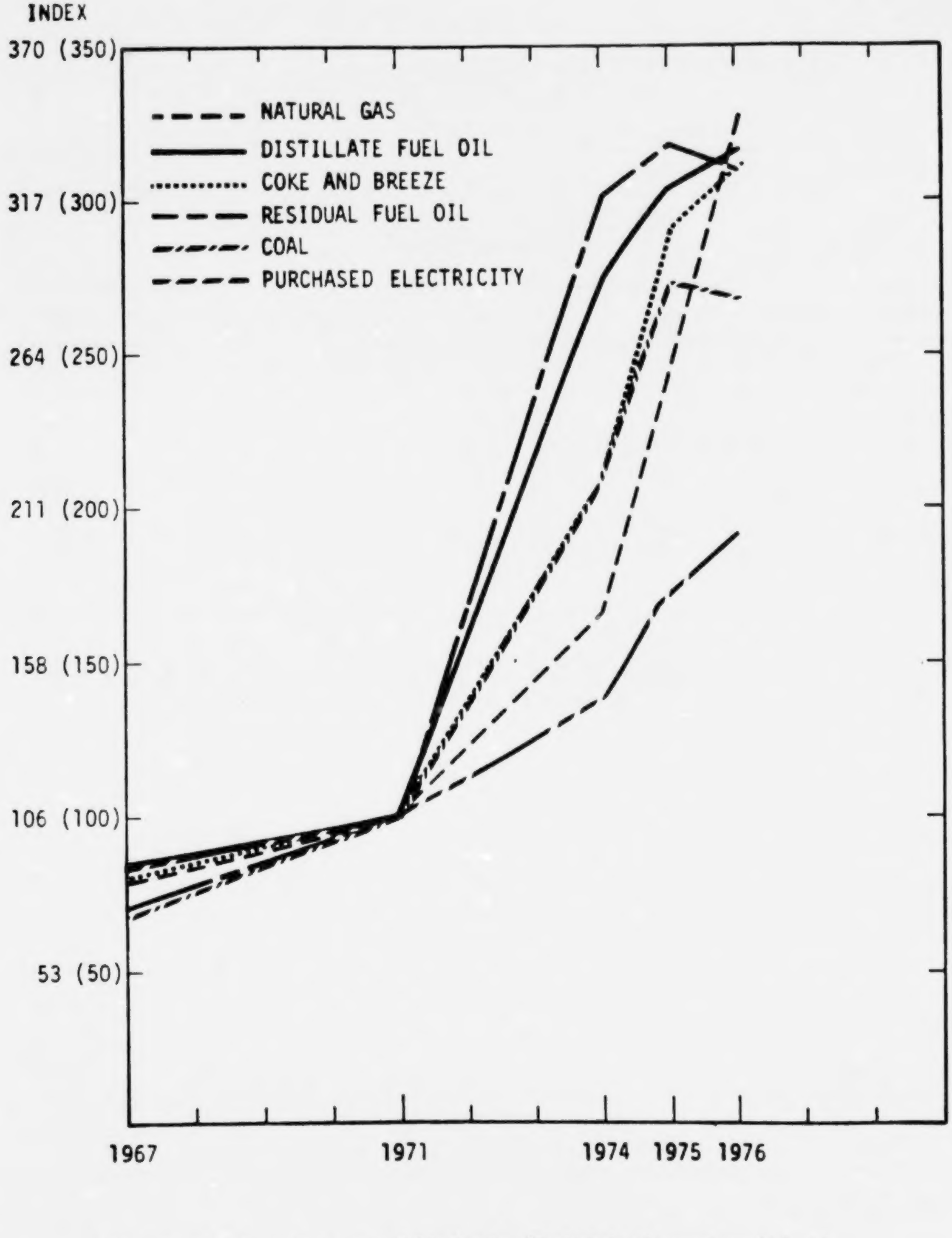

Figure 3.1-1. Cost per kilojoule (British thermal unit) of selected fuels and purchased electricity consumed by all manufacturing industries 1976, 1975, 1974, 1971, and 1967[7] (1971 = 100)

3.1.3 Future Energy Use

The major factors affecting the future growth of the boiler population are the economic growth of the nation, technological advancements in energy production and use, fuel use patterns, and energy and environmental regulatory trends.

Projections of fuel usage in the future are given in reports prepared by the Edison Electric Institute (EEI) and the Energy Information Administration (EIA). Results of the reports are included in the following subsection.

3.1.3.1 The EEI/EIA Projections--

The report issued by the EEI in 1976[8] analyzes the growth of energy use as it relates to economic growth. The report does not attempt to factor in the effects of forced fuel conversion on usage trends. Several scenarios are given to represent interactions of nine separate elements: (1) population, (2) agriculture, (3) growth of income and consumption, (4) mineral demand and supply, (5) energy demand and supply, (6) conservation and environment, (7) pricing policies, (8) capital requirements, and (9) relations with the rest of the world. By varying some of these elements, EEI formulates three scenarios of energy-demand growth: Case A--high economic growth; Case B--moderate economic growth; Case C--low (or no) economic growth. Case A is predicted to result in a 4 percent annual increase in U.S. energy demand by the industrial sector to the year 2000; Case B is predicted to result in a 3 percent annual increase; and Case C is predicted to result in only a 0.5 percent annual increase.

The EEI executive summary states: "To achieve greater energy independence, it will be necessary to make a basic shift from oil and natural gas to coal and nuclear fuels. Development of facilities to liquefy and gasify coal will complement this shift by enlarging the areas of consumption to be served by coal. Ultimately, oil and gas consumption will be limited by market pressures to those uses where coal and nuclear power are not feasible substitutes such as for petrochemical raw materials."[9]

The Energy Information Administration (EIA) issues an annual report to Congress. On the basis of its close contact with the DOE and the overall energy picture with respect to the National Energy Plan, the EIA has speculated on the future effects of the FUA in projecting total energy requirements by industry. A preliminary summary release of the annual report gives the following forecasts:[10]

> Coal production is projected to grow from 695 million tons [0.63 Tg] in 1977 to 1.3 to 1.6 billion tons [1.2 to 1.5 Pg] per year by 1990, with the growth rate of western coal about four times greater than eastern coal.
>
> Oil import requirements will decline slightly over the mid-term (1990) period, from 8.8 million barrels daily (MMBD) [1.4 million m^3/day] to between 5.9 and 8.3 MMBD [0.9 and 1.3 million m^3/day] in 1990.
>
> U.S. total energy consumption will grow at an annual rate ranging between 1.6 percent and 2.8 percent between 1977 and 1990, as compared to 2.6 percent annually over the 1962 to 1977 period.
>
> Electric utilities and industry will shift to coal and away from oil and natural gas as a result of the National Energy Act and rising world oil prices. Coal's portion of industrial energy consumption will increase from 17 percent in 1977 to between 18 and 23 percent in 1990. In electric utilities, coal's share will increase to between 52 and 58 percent in 1990, as compared to 45 percent in 1977.
>
> Energy prices will continue to rise faster than the rate of inflation over the mid-term, with electricity prices increasing more slowly and natural gas prices more rapidly than the prices of other fuels.

The further possible effects of NSPS for large coal-fired utility boilers and possible NSPS for industrial and commercial boilers are not factored into the projections.

3.1.4 Conclusions

Replacement of fuels of low sulfur content with coal will unavoidably increase the generation of sulfur oxides. In the past, the sulfur oxide control strategies could require the use of low sulfur fuels. With both the current energy situation and recent energy legislation, the control of SO_2 emissions by switching to lower sulfur fuels, such as natural gas and oil, is not a viable option.

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3.2 DETERMINING EMISSION REDUCTION NEEDS

This section summarizes the various air programs that may require control of sulfur oxides (SO_x). It briefly discusses each program, its emission reduction requirements, and its current status. It also provides information on the dispersion models available for estimation of the air quality impacts of sulfur dioxide (SO_2) emission sources.

3.2.1 Emission Regulations

This discussion deals with the basic regulations that apply to SO_2 emissions. These regulations are the State Implementation Plans (SIP's) and the New Source Performance Standards (NSPS). The SIP's are designed to attain and maintain the National Ambient Air Quality Standards (NAAQS) and to prevent the significant deterioration (PSD) of air quality. In addition, a discussion is provided concerning the future regulations that will be promulgated regarding the SIP requirements to protect and enhance visibility.

3.2.1.1 State Implementation Plans for the attainment and maintenance of the NAAQS--

The Clean Air Act of 1970 gave the Environmental Protection Agency (EPA) the responsibility and legal authority to control air pollution in the United States. Among the many responsibilities given to EPA was the establishment of NAAQS for those pollutants "the emissions of which, in the Administrator's judgement, cause or contribute to air pollution which may reasonably be anticipated to endanger public health or welfare; and the presence of which in the ambient air results from numerous or diverse mobile or stationary sources."[1] One of the pollutants included in this group was sulfur oxides measured as sulfur dioxide.

The Clean Air Act of 1970 also mandated that these NAAQS must be attained as expeditiously as practicable and that each state develop, adopt, and submit to EPA for approval a plan that provided for the attainment, maintenance, and enforcement of the NAAQS in every air quality control region (AQCR), as designated by EPA under Section 107(C) of the Act.

In developing its plan, each state determined (on the basis of current air quality levels) the degree of emission reduction required to attain or maintain the NAAQS within all areas of the state. Additionally, the state determined which air pollution sources must be controlled and to what extent, to accomplish the necessary emission reductions. The SIP then set forth the necessary emission limitations and timetables for compliance to ensure attainment and maintenance of the NAAQS.

Since the primary responsibility for development and enforcement of the SIP fell to the states and each plan was tailored to an individual state, the SO_2 regulations varied from state to state. They varied both in the units of measure in which the limitation on sulfur or SO_2 was expressed and in the equipment to which the regulations apply. In addition, some states have a uniform regulation for all sources of either combustion or process emissions, whereas other states have different emission limitations for various sources according to the fuel used, type of material processed, geographic location, size of the source, or type of source.[2]

In general, process regulations are of five types: (1) pounds of SO_2 emitted per hour; (2) pounds of total sulfur feed, expressed in pounds of sulfur per hour or pounds of sulfur emitted per pound of input sulfur; (3) pounds of SO_2 per ton of product; (4) flue gas concentrations of SO_2 (e.g. ppm); and (5) ground-level concentrations of SO_2 (e.g., ppm).[3]

Sulfur dioxide emissions from fuel combustion are usually regulated either by limiting the amount of sulfur or SO_2 emitted per unit heat input (nanograms SO_2/joule, pounds SO_2/million Btu) or by limiting the sulfur content of the fuel by weight. Sulfur dioxide emissions are also limited by restricting the flue gas concentration of SO_2 in parts per million or grains per cubic foot or by limiting the amount of SO_2 emitted per hour. A few states specify a ground-level or ambient concentration of SO_2 that cannot be exceeded. Additionally, a few states require a percent reduction of input sulfur and application of "reasonable or best available control technology" or "new proven technologies."

Some states or territories enforce their fuel combustion regulations on a boiler basis, others on a stack basis, and still others on a total plant basis. Depending upon the regulation, a source may be able to average its emissions over all boilers (or stacks) rather than ensuring that each boiler complies with the regulation.

Some states regulate specific fuel types. Other states have specific SO_2 regulations for various geographic areas. In some areas (e.g., Ohio) regulations have been promulgated to apply to specific plants. In a few states, the size of the source determines whether the source must comply with an SO_2 emission limitation and also determines the stringency of the limit. In most cases, source size is defined by the heat input rate measured in megawatts thermal (millions of Btu per hour). Other means of defining source size include kilograms (pounds) of steam generated per hour and megagrams (tons) of SO_2 emitted per hour. In some states, larger sources are controlled more stringently than smaller sources. Over half of the states have regulations incorporating more than one of the parameters discussed above. In addition, about 35 percent of the states have separate regulations for new sources.[4]

Finally, only a few states limit the emissions or the fuel quality as a maximum value averaged over a given time period. Most states indicate only that the emissions or sulfur content shall not exceed a maximum value. This type of regulation implies that compliance is instantaneous.[4]

In most areas, sources have complied with the SO_2 emission limitations, and considerable progress has been made in reducing the ambient levels of SO_2. In some areas, however, the national ambient air quality standards for SO_2 are still being violated. Because of this continuing nonattainment of SO_2 as well as other NAAQS's, Congress passed the Clean Air Act Amendments of 1977. These amendments required that the states evaluate the current air quality levels and pursuant to section 107(d), designate as "nonattainment areas" those areas in which levels of air pollution are above the national standards. Once these nonattainment areas were designated, the states were to develop a plan for attaining these standards as expeditiously as practicable, but no later than December 31, 1982. The attainment plans were scheduled for submission to EPA by January 1, 1979, and for EPA approval by July 1, 1979. If a state did not have an approved plan by July 1, 1979, certain limitations on funding and new source growth were to be invoked until the state developed and EPA approved an adequate plan. A list of nonattainment areas was published on March 3, 1978, with subsequent modifications for which states developed their attainment plans.[5]

In some of these areas, compliance with existing regulations will provide attainment of the national standards. In other areas more stringent emission limitations will be needed to attain the standard by December 31, 1982, as the Act requires. Since many of these state plans have not been approved, the types of new limits that must be met are unknown at this time. As these plans are approved, the existing state regulations summarized above are certain to be modified.

In addition to the control requirements affecting existing sources, the Clean Air Act Amendments of 1977 require the states to develop a permit program for new sources. As a minimum, this program must assure that all new sources with actual SO_2 emissions equal to or greater than 91 Mg (100 tons) per year and which cause or contribute to a violation of the NAAQS in an area designated as nonattainment must apply the Lowest Achievable Emission Rate (LAER). The LAER represents the most stringent emission limitation that is contained in any SIP for that particular class or category of source or the most stringent emission limitation achieved in practice by that particular class or category of source. In addition, no new source permit can be issued unless the state determines that by the time the new source is to commence operation either of the following will have occurred: (1) the total allowable emissions from existing and new sources will be sufficiently lower than the total emissions from existing sources under the applicable implementation plan prior to the application of the new sources so as to represent reasonable further progress toward attainment or (2) emissions from the new source will not cause or contribute to emissions levels that exceed those allowed under the SIP for new source growth. Also, the owner or operator of the new source must demonstrate that all major sources owned and operated by him within the state in which he wishes to construct are subject to emission limitations and are in compliance or on a schedule for compliance. The state must also be carrying out the provisions of the plan.[6]

3.2.1.2 State Implementation Plans for Prevention of Significant Deterioration--

In 1974, EPA issued regulations under the 1970 Clean Air Act for the prevention of significant air quality deterioration. These regulations establish a program for protecting areas with air quality better than that specified in the NAAQS.

Under EPA's regulatory program, clean areas of the nation could be designated under any of three "Classes." For particulate matter and sulfur oxides, specified numerical "increments" of net air pollution increase are permitted under each class up to a level considered to be "significant" for that area. Class I increments permit only minor air quality deterioration; Class II increments permit moderate deterioration; Class III increments permit deterioration to the level of the secondary NAAQS.

The EPA initially designated all clean areas of the Nation as Class II. States, Indian tribes, and officials having control over Federal lands (Federal land managers) were given authority to redesignate their lands to Class I or III status under specified procedures.

The initial area classification scheme was administered and enforced through a program of preconstruction and premodification permits for 19 specified types of stationary air pollution sources. No such air pollution source could begin construction or modification unless EPA (or a state) had found that the source's emissions would not exceed the numerical "increments" for the applicable Class and that the source would use best available control technology (BACT). The permit program applied to sources that had not "commenced construction," as defined in the regulation, by June 1, 1975.[7]

The 1977 Amendments to the Clean Air Act essentially ratified, extended, and generally made more stringent the PSD provisions promulgated in 1974. Basically the new Amendments require classification of all areas as Class I, II, or III. The air quality in each of these areas is allowed to deteriorate only by a specific amount or increment. The increments for each Class are presented in Table 3.2-1.[8] Except for the Class I areas listed in Figure 3.2-1 and the Northern Cheyenne Indian Reservation, the entire country is designated as Class II.

TABLE 3.2-1. AIR QUALITY INCREMENTS FOR THE PREVENTION OF SIGNIFICANT DETERIORATION[8]
($\mu g/m^3$)

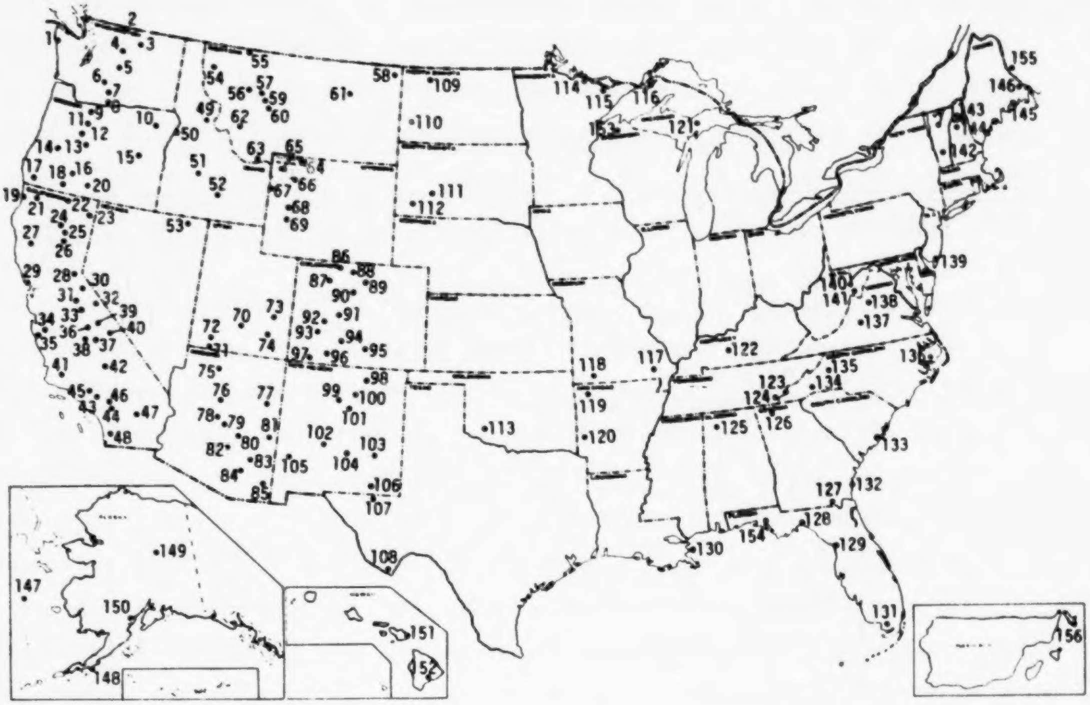
	Class I	Class II	Class III
SO_2 annual	2	20	40
24-hour	5	91	182
3-hour	25	512	700
TSP annual	5	19	37
24-hour	10	37	75

The 1977 Amendments designate the following areas as Class I areas and prohibit redesignation into either of the other two classes: 1) international parks, 2) national wilderness areas exceeding 20 million m^2 (5000 acres), 3) national memorial parks exceeding 20 million m^2 (5000 acres), and 4) national parks exceeding 24 million m^3 (6000 acres). Figure 3.2-1 is a map of the Class I areas.

The 1977 Amendments also required that each new or modified major emitting facility or major stationary source obtain a preconstruction permit. These amendments defined a major emitting facility as a stationary source of air pollutants in any of 28 specific source categories (listed in Table 3.2-2) that emit or have the potential to emit 91 Mg (100 tons) per year or more of any pollutant regulated under the Clean Air Act and as any other source (not specifically listed) that has the potential to emit 227 Mg (250 tons) per year or more of any pollutant regulated under this act.

On June 19, 1978, the EPA published regulations to implement the 1977 Amendments. These regulations state that no major stationary source may be constructed unless the following criteria are met: a permit is issued to that source; the owner or operator of the source demonstrates that the emissions from the operation will not cause or contribute to air pollution levels in excess of: maximum allowable increases (i.e., the increments for TSP and SO_2 established under Section 163 of the Clean Air Act), NAAQS in any region, or other applicable emission standards or standards of performance under the Clean Air Act; the proposed source is subject to the Best Available Control Technology for each pollutant it emits, which is subject to regulation under the Clean Air Act; and the owner or operator agrees to conduct such monitoring that may be necessary to determine what effect emissions of this proposed facility may have on air quality.

The regulations defined potential to emit as the capability at maximum capacity to emit a pollutant in the absence of air pollution control equipment. Annual potential will be based on the maximum rated capacity of the source unless the source is subject to enforceable permit conditions that limit the annual hours of operation. Enforceable permit conditions on the type or amount of materials combusted or processed may be used in determining the potential emission rate of a source. The regulations also



1. Olympic
2. Pasayton
3. North Cascades
4. Glacier Park
5. Alpine Lakes
6. Mount Ranier
7. Goat Rocks
8. Mt. Adams
9. Mt. Hood
10. Eagle Cap
11. Mt. Jefferson
12. Mt. Washington
13. Three Sisters
14. Diamond Peak
15. Strawberry Mtn.
16. Crater Lake
17. Kalmiopsis
18. Mountain Lakes
19. Redwood
20. Gearhart Mtn.
21. Marble Mtn.
22. Lava Beds
23. South Warner
24. Thousand Lakes
25. Lassen
26. Caribou
27. Yolla Bolly Middle Eel
28. Desolation
29. Pt. Reyes
30. Mokelumne
31. Emigrant
32. Hoover
33. Yosemite
34. Pinnacles
35. Ventana
36. Kaiser
37. Kings Canyon
38. Sequoia
39. Minarets
40. John Muir
41. San Rafael
42. Dome Land
43. Cucamonga
44. San Jacinto
45. San Gabriel
46. San Gorgonio
47. Joshua Tree
48. Aqua Tibia
49. Selway-Bitterroot
50. Hell's Canyon
51. Sawtooth
52. Craters of the Moon
53. Jarbridge
54. Cabinet Mtns.
55. Glacier
56. Mission Mtn.
57. Bob Marshall
58. Medicine Lake
59. Scapegoat
60. Gates of the Mountain
61. UL Bend
62. Anaconda Pintler
63. Red Rock Lake
64. North Absaroka
65. Yellowstone
66. Washakie
67. Grand Teton
68. Fitzpatrick
69. Bridger
70. Capitol Reef
71. Bryce Canyon
72. Zion
73. Arches
74. Canyonlands
75. Grand Canyon
76. Sycamore Canyon
77. Petrified Forest
78. Pine Mt.
79. Mazatzal
80. Sierra Ancha
81. Mt. Baldy
82. Superstition
83. Galiuro
84. Saguaro
85. Chiricahua
86. Mt. Zirkel
87. Flat Tops
88. Rawah
89. Rocky Mtn.
90. Eagles Nest
91. Maroon Bells Snowmass
92. West Elk
93. Black Canyon
94. La Garita
95. Great Sand Dunes
96. Weminuche
97. Mesa Verde
98. Wheeler
99. San Pedro Parks
100. Pecos
101. Bandelier
102. Bosque del Apache
103. Salt Ck.
104. White Mtn.
105. Gila
106. Carlsbad Caverns
107. Guadalupe
108. Big Bend
109. Lostwood
110. Theodore Roosevelt
111. Badlands
112. Wind Cave
113. Witchita Mtns.
114. Voyageurs
115. Boundary Waters
    Canoe Area
116. Isle Royale
117. Mingo
118. Hercules Glades
119. Upper Buffalo
120. Caney Creek
121. Seney
122. Mammoth Cave
123. Great Smokey Mtns.
124. Joyce Kilmer-Slickrock
125. Sipsey
126. Cohutta
127. Okefenokee
128. St. Marks
129. Chassahowitzka
130. Breton
131. Everglades
132. Wolf Island
133. Cape Romain
134. Shining Rock
135. Linville Gorge
136. Swanquarter
137. James River Face
138. Shenandoah
139. Brigantine
140. Dolly Sods
141. Otter Creek
142. Lye Brook
143. Great Gulf
144. Presidential Range
    Dry River
145. Acadia
146. Moosehorn
147. Bering Sea
148. Simeonof
149. Mt. McKinley
150. Tuxedni
151. Haleakala
152. Hawaii Volcanoes
153. Rainbow Lake
154. Bradwell Bay
155. Roosevelt Campobello
    International Park
156. Virgin Islands

Figure 3.2-1. Mandatory Class I areas for PSD.

TABLE 3.2-2. MAJOR SOURCES SUBJECT TO PSD REVIEW

Specific sources with potential emissions >91 Mg/yr (100 tons/yr)

- Fossil fuel-fired steam electric plants [>73 MW thermal (>250 million Btu/h)]
- Coal-cleaning plants (thermal dryers)
- Kraft pulp mills
- Portland cement plants
- Primary zinc smelters
- Iron and steel mill plants
- Primary aluminum ore reduction plants
- Primary copper smelters
- Municipal incinerators [2.6 kg/s (>250 tons/day)]
- Hydrofluoric acid plants
- Sulfuric acid plants
- Nitric acid plants
- Petroleum refineries
- Lime plants
- Phosphate rock processing plants
- Coke oven batteries
- Sulfur recovery plants
- Carbon black plants (furnace process)
- Primary lead smelters
- Fuel conversion plants
- Sintering plants
- Secondary metal production facilities
- Chemical process plants
- Fossil-fuel boilers [>73 MW thermal (>250 million Btu/h)]
- Petroleum storage and transfer facilities [capacity >47,700 m^3 (>300,000 bbl)]
- Taconite ore processing facilities
- Glass-fiber processing plants
- Charcoal production facilities

Any other source with potential emissions >227 Mg/yr (>250 tons/yr) provide that only certain sources would receive a full PSD review. The detailed review would only be provided to those sources with allowable emissions equal to or greater than 45 Mg (50 tons) per year, 455 kg (1000 pounds) per day, or 45 kg (100 pounds) per hour and to those sources that would impact a Class I area or an area where the increment is known to be violated. The detailed review includes an assessment to ensure that the source has applied BACT and that the source will not violate any applicable increment or NAAQS.[8]

Best available control technology is determined on a case-by-case basis for each pollutant regulated under the Act and must represent an emission limitation based on the maximum degree of reduction (taking into account energy, environmental, and economic impacts, and other costs). In no event shall application of BACT result in emissions that would exceed those allowed under an applicable NSPS or National Emission Standards for Hazardous Air Pollutants (NESHAPS). The NESHAPS are set for those pollutants to which no ambient air quality standard is applicable and which, in the judgment of the Administrator, cause or contribute to air pollution that may reasonably be anticipated to result in an increase in mortality or an increase in serious irreversible or incapacitating reversible illness.

The 1977 Amendments also provide protection for Class I areas in addition to the increments. The protection of "air quality related values" is a large factor in determining whether a source may be granted a permit if it would impact a Class I area. If the Federal land manager responsible for the Class I area demonstrates that emissions from the proposed new source would have an adverse impact on "the air quality related values" of the area (even if the Class I increments would not be exceeded), a permit would not be issued. Some special exemptions from this review process are given in the regulations of June 19, 1978. Visibility is an example of an air quality related value. It is likely that the potential adverse impact on visibility will act as the primary triggering mechanism for a review of air quality related values; other values, such as vegetative impacts and climatological change, may also be identified.[9]

Many industrial and environmental groups petitioned the United States Court of Appeals of the District of Columbia Circuit to review substantiative portions of the June 1978 revised regulations. On June 18, 1979, in

The Alabama Power Company v. Costle (13 ERC 1225), the Court issued a decision that upheld some of the provisions of the June 1978 regulations and overturned others. In its opinion, the Court summarized its ruling and promised a supplemental comprehensive opinion at a later date. (The court issued its final opinion on December 14, 1979.) On September 5, 1979, following the court's mandate, the EPA proposed certain changes in the June 19, 1978, regulations to make the PSD requirements consistent with the June 1979 summary decision in Alabama Power. The proposed changes included:

Potential to emit
Fugitive emissions
Major modification
Preconstruction notice
Baseline definition
Ambient monitoring
De minimis levels

Each of these changes under the proposed regulations is discussed below.

Potential emissions would be determined after application of emission controls and would be calculated using maximum annual rated capacity, year-round hours of operation, and any enforceable permit condition on the material combusted or processed.

Fugitive emissions would be excluded from a source's annual potential emissions unless these emissions are from the industrial source categories listed below:

Coal-cleaning plants
Kraft pulp mills
Portland cement plants
Primary zinc smelters

Iron and steel mill plants
Primary aluminum ore reduction plants
Primary copper smelters
Municipal incinerators

Hydrofluoric acid plants
Sulfuric acid plants
Nitric acid plants
Petroleum refineries

Lime plants
Phosphate rock processing plants
Coke oven batteries
Sulfur recovery plants

Carbon black plants
Primary lead smelters
Fuel conversion plants
Sintering plants

Secondary metal production plants
Chemical process plants
Fossil fuel-fired boilers
Petroleum storage and transfer units

Taconite ore processing plants
Glass fiber processing plants
Charcoal production plants
Fossil fuel-fired steam electric plants

Any other source category being regulated under Section 111 or 112 of the Act at the time of the applicability determination would also be included in the above list.

The current regulations subject a modified source to review if it is one of the 28 source categories with emission increases above 91 Mg (100 tons) per year or if it is any other source with increases above 227 Mg (250 tons) per year; associated emission reductions were not allowed to exempt the source from PSD review, but reductions that offset the increase and prevented a net increase were allowed to be used to avoid BACT review. Under the proposed regulations, any modification to a major source would be subject to PSD review if the modification would cause a net increase in the source's potential to emit. The proposal also states that emission increases offset entirely by contemporaneous emission reductions would not be considered a modification. However, if a major stationary source modifies its pollutant emissions so that the net increase in any pollutant would be above the proposed *de minimis* levels, it would be subject to PSD review for all the pollutants it emits above the *de minimis* levels as a result of the modifications.

The September 5, 1979, proposal revised the definition of baseline and established the baseline date as the time of the first completed permit application, after August 7, 1977, within an Air Quality Control Region designated as either attainment or unclassified.

More ambient monitoring would be required before and after construction, as a result of the proposal, for all pollutants regulated under the Act--not just the criteria pollutants.

The regulations also proposed to exempt, on a pollutant-specific basis, major modifications and new sources from the BACT and air quality impact assessment requirements, if the emissions of a specific pollutant are below the de minimis level. The de minimis air quality levels are to be used as guidelines for exempting sources from PSD air quality analysis on a pollutant-specific basis, if the emissions are above the proposed de minimis emissions levels.[10]

The PSD program is currently being implemented for the most part by EPA; however, the states are required to develop their own PSD programs consistent with the requirements published by EPA.

3.2.1.3 State Implementation Plans for Visibility--

The Clean Air Act Amendments of 1977 under Section 169A require the EPA Administrator to promulgate regulations setting forth guidelines for the development of SIP's to remedy existing problems and prevent future visibility impairment in those mandatory Class I Federal areas where visibility is an important value. The current assessment of Class I areas where visibility is an important value includes all mandatory Class I Federal areas except two, Bradwell Bay (Florida) and Rainbow Lake (Wisconsin).

The SIP revisions will include an evaluation of existing major sources and a requirement that those major sources which started operation after August 6, 1962, and which cause or contribute to significant visibility impairment in the mandatory Class I Federal areas install and operate Best Available Retrofit Technology. These sources, which are listed in Table 3.2-2, have the potential to emit 227 Mg (250 tons) per year. The visibility regulations were proposed on May 23, 1978 (45 FR 34762)

3.2.1.4 New Source Performance Standards (NSPS)--

The Clean Air Act of 1970 in Section 111 requires the EPA to develop NSPS. The overriding purpose of Section 111 is to prevent the general occurrence of new air pollution problems by requiring the installation of best available controls during initial construction. Performance standards for new sources are designed to allow industrial growth without undermining air quality management goals. The NSPS are established at a national level to provide uniformity and consistency to the requirements that a new source must meet, regardless of location.

The term "standard of performance" shall reflect the degree of emission limitation and the percentage reduction achievable through the application of the best technological system of continuous emission reduction which the Administrator determines has been adequately demonstrated (taking into consideration the cost of achieving such emission reduction, any nonair quality health and environmental impact, and energy requirements). In addition, the standards are to be established only for significant sources (i.e. greater than 100 tons/yr potential emissions).[11]

The NSPS apply only to new sources. A new source is defined as any stationary source on which construction is started after publication in the Federal Register of the proposed NSPS for that source type. It is the intent of the Clean Air Act that eventually NSPS will be promulgated for all significant emission-producing sources. Additionally, any physical or operational change to an existing facility that results in an increase in the emission rate to the atmosphere of any pollutant to which a standard applies shall be considered a modification within the meaning of Section 111 of the Act. Upon modification, an existing facility shall become an affected facility for each pollutant to which a standard applies and for which there is an increase in the emission rate to the atmosphere.

In addition, when an existing facility is reconstructed, it becomes subject to an applicable NSPS irrespective of any change in emission rate. Reconstruction involves the replacement of components of an existing facility to such an extent that (1) the fixed capital cost of the new components exceeds 50 percent of the fixed capital cost that would be required to construct a comparable entirely new facility and (2) it is technologically and economically feasible to meet the applicable standards set forth in 40 CFR Part 60.

Implementation and enforcement of NSPS may be delegated to the states; however, until the state submits a satisfactory plan, EPA is required to enforce the NSPS.

As of January 1, 1979, EPA had promulgated NSPS regulations covering 27 new source categories. Of these only six source categories include limits for SO_2:

1) Fossil-fuel-fired steam generators of capacity greater than 73 MW thermal (250 x 10^6 Btu/hr)

2) Sulfuric acid plants

3) Petroleum refineries

4) Primary copper smelters

5) Primary zinc smelters

6) Primary lead smelters.

The Clean Air Act Amendments of 1977 reaffirm the NSPS process set forth by the 1970 act and require that EPA significantly expand the coverage of NSPS over the next 4 years. The EPA is directed to identify all categories of stationary sources that are not among the list of source categories regulated under NSPS. The Clean Air Act provides some guidance in determining the priorities for promulgating standards for certain categories of major stationary sources. The Administrator shall consider the following:

- The quantity of air pollutant emissions that each such category will emit, or will be designed to emit
- The extent to which each such pollutant may reasonably be anticipated to endanger public health or welfare
- The mobility and competitive nature of each such category of sources and the consequent need for nationally applicable new source standards of performance.

Given the priorities of the 1977 Act, EPA undertook a study[12] to establish priorities for setting NSPS. The results of this study culminated in the publishing of the final priority list for NSPS in the August 21, 1979, Federal Register.

Additionally, the 1977 amendments provide some guidance on the desired schedule for developing standards.[13] By August 1980, NSPS must be established for at least one-quarter of the categories listed in the August 21, 1979, Federal Register notice. By August 1981, standards must be promulgated for at least three-quarters of the listed categories, and for all listed categories by August 1982.

The 1977 amendments also introduce an important provision relating to NSPS for new fossil-fuel-fired stationary sources, Section 111(a)(1)(A). Formerly such sources were subject only to the customary emission limitations expressed as nanograms per joule (pounds per million Btu). Many fossil-fuel-fired stationary sources turned to firing of low-sulfur coal and similar fuels from western mines in order to meet the emission limitations. The 1977 amendments require that new and modified fossil-fuel-fired stationary sources achieve a percentage reduction in emissions in addition to meeting emission limitations. By requiring a specified percentage reduction, this provision appears to eliminate the incentive for burning fuels of naturally low sulfur content and requires these sources to adopt technological controls.[14]

3.2.2 Dispersion and Dispersion Modeling

As stated earlier, an application for a preconstruction permit for a new source or a major modification to an existing source must include an assessment of the air quality impact of the emissions from the proposed source. For a source that is to be located in an attainment area, it is necessary to satisfy the requirements for the PSD. These requirements include showing that the source will not cause violations of applicable NAAQS nor will the maximum impact of the source exceed the remaining PSD increment (Table 3.2-1). Further, it must be shown that the new source will not significantly impact any area that has been designated as nonattainment. Here a significant impact is construed to be the same as the maximum PSD increments for a Class I area (i.e., for SO_2, 2 $\mu g/m^3$ annually, 5 $\mu g/m^3$ in 24 hours, and 25 $\mu g/m^3$ in 3 hours, not to be exceeded more than once per year at any receptor).

A new source of SO_x emissions that is to be constructed in a nonattainment area must demonstrate that there will be a net air quality improvement within the nonattainment area after the new source becomes operational. It must also be shown that the new source will not cause violations of the NAAQS, nor exceed the allowable PSD increments in any nearby attainment area.

The Federal regulation relative to the PSD (40 CFR 52.21) specifies that "all estimates of ambient concentrations required under this section shall be based upon applicable air quality models, data bases, and other requirements specified in the Guideline on Air Quality Models."[15] The guideline includes a brief description of currently available dispersion models and their applicability to individual and multiple sources. This guideline should be followed in any analysis pertinent to sources of SO_x emissions.

Congress recognized the state-of-the-art nature of currently available dispersion models and the need to maintain consistency in the application of these models. To this end Section 320 of the Clean Air Act, as amended August 1977, requires that the Administration of the EPA conduct periodic conferences on air quality models. The Act specifically provides that such conferences provide participation by the National Academy of Sciences, state and local air pollution control agencies, and other appropriate agencies such as the National Science Foundation, the National Oceanic and Atmospheric Administration and others. These conferences will provide a basis for the updating of the Guidelines on Air Quality Models.

Section 123 of the Clean Air Act, as amended in 1977, limits the credit of the physical stack height for determining control requirements to that height required to avoid excessive concentration caused by "atmospheric downwash, eddies, and wakes." The EPA has proposed to define that height as H + 1.5 L, where H is the height of a nearby building and L is the lesser dimension of the height or width of that building, or the height that is demonstrated as necessary through physical modeling or field studies.

REFERENCES FOR SECTION 3.2

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3. Analysis of Final State Implementation Plans--Rules and Regulations. APTD 1334. July 1972. pp. 9-11.
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12. Argonne National Laboratory. Priorities for New Source Performance Standards Under the Clean Air Act Amendments of 1977. (Draft) February 28, 1978. pp. 59-64.
13. Ref. 12, pp. 1, 2.

14. Truitt, T.H., and R.M. Hall. Practical Environmental Law. Federal Publications, Inc. pp. 42-54.

15. Guideline on Air Quality Models. U.S. Environmental Protection Agency. Research Triangle Park, N.C. EPA-450/2-78-027. April, 1978. 48 pp.

3.3 TECHNICAL CONSIDERATIONS

3.3.1 Introduction

When attempting to reduce SO_2 emissions from an existing source or to prevent or minimize potential SO_2 emissions from a proposed facility, one must be aware of local, state, and Federal standards limiting SO_2 emissions. For example, new stationary source performance standards limiting SO_2 emissions from power plants may be found in the Federal Register.[1]

Many processes are available for the removal of SO_2 from both process and combustion sources. These processes involve direct conversion of SO_2 streams to sulfuric acid, sulfur, and liquid SO_2 for sale or disposal; absorption of SO_2 in ammonia liquors, which can produce a salable ammonium sulfate fertilizer product; absorption of SO_2 from lower concentration streams with organic or inorganic reagents to produce a stronger, usable SO_2 stream for conversion to salable sulfur products; or the absorption of SO_2 by various alkaline reagents in nonregenerable systems. Many such systems are used in the utility[2] and industrial[3] sectors.

3.3.2 Determination of the Required SO_2 Removal

The magnitude of SO_2 removal required can be obtained by comparing existing SO_2 emission levels with SO_2 control regulations. For an existing source, emission testing is performed to determine the degree of SO_2 control required. For major modifications to existing installations, which are expected to yield increased sulfur oxide emissions, or for new plants, background sampling is required to establish local environmental quality. The sampling, measurement, and analysis techniques practiced by the regulatory/control agency having jurisdiction over the emission source should be used. An approximate method to determine SO_2 emissions from a combustion source is to use the appropriate emission factor.[4] For example, the amount of uncontrolled SO_2 emissions from a new coal-fired boiler for a specific heat input rate can be determined by knowing the sulfur content of the coal to be fired and the heating value of the coal, and by assuming the fractional conversion (such as 0.95) of sulfur in the coal to SO_2.[5] Comparing the peak uncontrolled value of SO_2 emissions with the applicable regulation gives the required SO_2 removal. The necessary SO_2 removal for existing sources can be determined similarly.

3.3.3 Gas Stream Characteristics

The next step is to check the characteristics of the gas stream to be treated.

In addition to sulfur oxides, the chemical composition of volatilized combustion products in the gas (such as NO_x, chlorides, fly ash, etc.) should be estimated in light of current and projected removal requirements.

The moisture content and temperature of inlet flue gas dictates the adiabatic saturation temperature of the gas stream and determines the amount of water that evaporates when the gas is cooled in either an SO_2 absorber or a wet particulate scrubber. The inlet gas temperature also affects the decision on whether the scrubber or absorber should be lined and what type of liner should be used.

The volume of the flue gas and the desired gas velocity in the flue gas desulfurization (FGD) train largely determine the dimensions of the particulate scrubber (if one is needed) and the SO_2 absorber. Furthermore, the availability of space for such an installation can influence the design.

The erosive properties of the inlet flue gas and its corrosiveness should be determined. The erosive characteristics can affect the equipment upstream of the FGD system (such as a forced-draft fan) and can have a significant effect on the downstream equipment that handles the gas stream. Stress corrosion caused by the high chloride content of some gas streams is crucial in selecting reliable materials of construction for the SO_2 absorber.

The electrical characteristics of the fly ash particles in the gas, such as the resistivity and the dielectric constant, play an important role when an electrostatic precipitator (ESP) is used for particulate collection prior to SO_2 removal.

3.3.4 SO_2 Removal Processes

As noted earlier, there are basically two choices in SO_2 removal processes: either use the SO_2 stream directly in a process for conversion to a sulfur product for use, sale, or disposal (such as sulfuric acid, sulfur, or liquid SO_2); or absorb the SO_2 in processes designed to produce an upgraded SO_2-concentration stream or a product for disposal.

The systems that produce a sulfur product directly may be typified by sulfuric acid plants in use in the nonferrous smelter industry (see Section 5.1), sulfur-reduction units in use in the petroleum industry (see Section 5.3), and dimethyl aniline (DMA) scrubbing units also in use in the nonferrous smelter industry. Sulfur product processes also are used in conjunction with weaker SO_2 stream removal processes where the absorbent is regenerated. The number of units, which may be referred to as flue gas desulfurization processes, that absorb SO_2 from process or combustion streams, for ultimate upgrading or disposal is much greater than those that directly produce a sulfur product.

There are four major categories of SO_2 removal (FGD) processes: nonregenerable, regenerable, wet, and dry. Nonregenerable processes produce either sludge or waste liquor that must be disposed of in an environmentally acceptable manner. Regenerable processes involve absorbent regeneration and production of elemental sulfur or a sulfur compound for sale or disposal; the byproduct may be marketable SO_2, elemental sulfur, or sulfuric acid.[6] Wet processes may require stack gas reheating to achieve the necessary plume buoyancy and to avoid corrosion problems; particulate removal, if required, is achieved prior to SO_2 removal. Dry processes generally do not require stack gas reheating and often simultaneously remove particulate matter and SO_2.

Wet lime/limestone FGD processes are most widely used in the utility sector. These processes can have scaling and plugging problems, which have been reduced as knowledge of chemical processes and as operating experience have been obtained. The primary advantage of these processes is the low reagent cost. System reliability and SO_2 removal capability can vary. Details are available on the operation of existing systems and SO_2 removal efficiencies achieved by these processes.[2]

Wet, sodium-based, nonregenerable FGD processes are most widely used in the industrial sector. Operating histories have generally been good. Sulfur dioxide removal efficiencies greater than 90 percent have been achieved by many installations.[3] The advantages of sodium-based processes are that SO_2 absorption is achieved by a clear alkaline solution and the reaction product is soluble. This eliminates scaling and plugging problems found in many calcium-based processes. The disadvantage is a significantly higher cost for the reagent than for lime or limestone.

The selection of an FGD system is influenced by whether the application is new or retrofit (an addition to the existing plant). In retrofit applications, space constraints and other site-specific factors are crucial to the installation of an FGD system.

A nonregenerable process produces throwaway sludge or waste liquor. As a result, the air pollution control problem can lead to both water pollution control and solid waste disposal problems. A 500-MW power plant firing coal with 3.5 percent sulfur and 14 percent ash [with a heat content of 27,924 kJ/kg (12,000 Btu/lb)] and employing a lime FGD system with 90 percent absorbent utilization and 80 percent SO_2 removal can generate 104,000 Mg/yr (115,000 tons/yr) of ash and 98,000 Mg/yr (108,000 tons/yr) of sulfur-based sludge (dry basis).[7] The disposal of these waste streams can require a large lined pond and further treatment.[8]

A nonregenerable FGD system can operate in an open- or closed-loop mode with respect to water usage. Current water pollution control legislation requires closed-loop operation. In a closed-loop system, it is necessary to control the makeup water flow at a level to avoid aqueous discharge and insufficient water for proper operation. Maintaining the proper water balance is critical in areas with limited availability of water.

In addition to SO_2 removal, the source may require a particulate collection device such as an ESP, fabric filter (baghouse), or wet scrubber. The choice of a particulate removal system is often determined by the physical and chemical characteristics of the fly ash and by whether particulate control devices are currently used.[9]

3.3.5 Control Equipment Alternatives

3.3.5.1 Particulate Control Devices--

Electrostatic precipitators, baghouses, and wet particulate scrubbers are used to remove particulate matter in order to meet emission standards for a source. The particulates not removed ahead of the FGD system can be removed in a properly designed absorber. The reagent for SO_2 absorption, however, can become contaminated, which increases the system blowdown and operating cost. When an ESP is used for particulate removal and upgrading of existing facilities is needed, the various alternatives include conditioning the flue gas, reducing the temperature of the flue gas stream, and installing additional plate area for particulate collection.

3.3.5.2 Presaturator--

Most FGD system suppliers prequench the gas before it enters the absorber so that the absorber lining (if used) is not exposed to a high temperature gas stream and the area of the wet/dry interface is minimized. Quenching may be done in a separate venturi stage in the inlet duct or inside the main absorber (especially in a horizontal absorber).

3.3.5.3 Types of SO_2 Absorbers[10,11]--

Flue gas desulfurization system suppliers offer a wide variety of absorbers: spray tower, packed tower, tray tower, or venturi; vertical or horizontal design; single-stage or two-stage construction; and cocurrent, countercurrent, or crossflow operation. The tradeoffs are simplicity, easier maintenance, and possibly higher reliability, contrasted with a more sophisticated absorber system with better SO_2 removal capability and absorbent utilization.

A spray absorber has no internals except spray nozzles. The mass transfer capability is not as good in spray absorbers as in packed or tray absorbers, but this can be offset by using a high liquid-to-gas ratio (L/G). A crossflow (horizontal) absorber is a special type of spray absorber.

A packed absorber may have mobile or fixed packing; fixed packing can be of various types. Packing improves mass transfer and allows the absorber to be operated at a lower L/G ratio; however, packing makes the absorber more subject to solids deposition, scaling, and plugging.

Tray absorbers consist of one or more trays mounted transversely inside the shell. The mass transfer capability is higher for tray absorbers than for spray absorbers. The overall effect is a multiple countercurrent contactor for the gas and liquid streams.

A venturi scrubber-absorber can collect particles with high efficiency; however, mass transfer capabilities are limited because of limited cocurrent gas-liquid contact time.

3.3.5.4 Materials of Construction--

The most important consideration in FGD system design is the selection of materials of construction. Low pH, high chloride, and presence of erosive solids complicate the selection of materials of construction. At high chloride levels (>30,000 ppm) in the recirculation loop, the use of reasonably priced, unprotected material is questionable because of chloride stress corrosion. Stainless steel can be used at average chloride levels (3000 to 5000 ppm). A number of coating materials have been tried, each having positive and negative features; no liner can be used in all applications. Site-specific considerations will dictate the type of liner that can be used. Process conditions determine what materials of construction should be chosen for other pieces of process equipment.[12,13]

3.3.6 Cost of Control

The cost of FGD systems is an area of considerable interest and substantial controversy. Many studies have been made to estimate capital and annual costs.[14,15,16]

Capital costs consist of direct costs, indirect costs, contingency costs, and other capital costs. Direct costs include the bought-out cost of equipment, the cost of installation, and site development. Indirect costs include interest during construction, contractor's fees and expenses, engineering, legal expenses, taxes, insurance, allowance of startup, and spares. Contingency costs include those costs resulting from unforeseen sources. Other capital costs include the nondepreciable items of land and working capital. The prefabricated equipment for a typical nonregenerable process includes fans and motors, ductwork, reheaters (if required), SO_2 absorbers, tanks and agitators, and pumps and motors. The cost of SO_2 absorbers is a major capital expense that may vary from 50 to 85 percent of the total installed cost of the equipment.

Annual costs consist of direct costs, fixed costs, and overhead costs. Direct costs include the cost of raw materials, utilities, operating labor and supervision, and maintenance and repairs. Fixed costs include depreciation, interim replacement, insurance, and taxes and interest on borrowed capital. Overhead costs include plant and payroll expenses.

Various sources are available to estimate the capital and annual costs of the SO_2 control system selected.[14,15,16,17]

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3.4 ENVIRONMENTAL AND ENERGY IMPACTS

This subsection discusses the environmental impacts of sulfur dioxide removal and the attendant energy impacts. The streams involved are the cleaned flue gas from coal combustion, the liquid portion of the scrubber/absorber purge, and any sludge generated.

3.4.1 Air Quality

The primary air quality impact of a flue gas desulfurization (FGD) system is the reduction of SO_2 in the exit gas stream. As discussed in depth in Section 4.2, FGD systems have demonstrated the capability of removing in excess of 90 percent of SO_2 emissions from combustion flue gas streams. This reduction in SO_2 is also reflected in the reduction of secondary sulfates, which are formed by the oxidation of the SO_2.

As SO_2 emissions are reduced, the impact of sulfuric acid and sulfate salts resulting from the chemical transformation of SO_2 in the atmosphere (secondary sulfates) is reduced; however, the amount of primary sulfates (sulfuric acid mist, sulfur trioxide aerosol, and sulfate salts) emitted directly as emissions from combustion sources can increase.[1,2] An air pollution control system such as an FGD system changes the characteristics of the gas stream. The gas becomes saturated with water vapor and is adiabatically cooled. The sulfur oxides in the flue gas after the FGD system can combine with water vapor to generate a fine aerosol of sulfurous and sulfuric acid. The sulfurous and sulfuric acid mist emitted from an absorber can produce secondary sulfates. It is generally necessary to reheat the treated flue gas to increase the plume buoyancy; this improves the dispersion of mist in the air.

In some cases, the SO_2 absorber also emits fine particulate matter that can be attributed either to poor removal efficiency of a particulate removal device or to particulates generated in the absorber. These particulates are solids present in the absorbent that are carried over from the absorber. The fine particulates emitted to the air can increase the opacity of the plume. Proper control of process conditions, improved mist elimination design, and improved efficiency of particulate removal devices for fine particulates can minimize the problem.

3.4.2 Water Quality

An FGD system generates liquid waste streams mainly as a purge from different points in the system (e.g., the quencher loop) and as supernatant liquor from the effluent stream. These liquid waste streams can contain significant amounts of total dissolved solids (TDS) and small, but significant, amounts of trace elements. Table 3.4-1 compares the chemical constituents of liquid waste streams from nonregenerable FGD systems with the National Interim Primary Drinking Water Regulation (NIPDWR).[3] The ratios of constituent concentrations to water criteria are given for ranges of various constituents of the samples analyzed.

TABLE 3.4-1. COMPARISON OF WASTE LIQUOR WITH DRINKING WATER CRITERIA[3]

NIPDWR drinking water criteria, mg/liter		Range of all samples[a]
As	0.05	<0.8 - 2.8
Cd	0.01	0.4 - 11
Cr	0.05	0.22 - 5
Pb	0.05	0.2 - 6.6
Mg	0.002	0.03 - 2.5
Se	0.01	0.28 - 20
F	~2	<0.5 - 5
TDS	500	6.6 - 48.5
pH (actual values)[b]		6.7 - 12.2

[a] Actual concentration/criteria concentration; unitless number.

[b] EPA-proposed secondary regulation is 6.5 to 8.5.

Table 3.4-1 shows that concentrations of all elements and the TDS and pH exceed the drinking water criteria. Although trace elements are not eliminated as a matter of concern by these data, there are indications that in many cases the concentrations are quite low and that the primary item of concern may generally be the concentration of dissolved solids and, in some cases, pH.[3]

3.4.3 Solid Waste

Under the provisions of the Resource Conservation and Recovery Act (RCRA) of 1976, the Environmental Protection Agency (EPA) has been directed to provide regulations and guidance to control the disposal of hazardous and nonhazardous wastes including solid waste, which includes air pollution control sludges.

The sludge and ash generated by a nonregenerable FGD system can require a large disposal area. It has been estimated that the amount of solid waste (ash and sludge) produced by a 500-MW power plant firing a 3.5 percent sulfur coal and having a limestone scrubbing system is 211,380 dry Mg/yr (233,000 dry tons/yr) or 298,500 m^3 (242 acre-ft) by volume.[4]

The solid wastes produced as a result of using regenerable processes are approximately 50 percent of those from nonregenerable processes. The wastes are primarily ash and are nearly independent of the regenerable process.[5]

Table 3.4-2 presents the concentrations of various sludge constituents from nonregenerable FGD systems.[6] The trace element content in an FGD sludge is a direct function of the combustion products of coal. Fly ash can represent the major source of trace elements in sludge for all but the most volatile elemental species (e.g., mercury and selenium) that are scrubbed from flue gases.[6] The FGD sludge may be treated chemically by several processes and often can be used in landfill applications. It has been shown that sludges chemically treated by commercially available processes can be disposed of in an environmentally sound manner and that the disposal site can be reclaimed as a structural landfill. The EPA considers permanent land disposal of raw (unfixated) sludge to be environmentally unsound. Although EPA has no regulatory authority to prevent raw sludge disposal, EPA anticipates states and local jurisdictions to require treatment of sludge.[7]

In regenerable processes, the SO_2 in the flue gas is absorbed and subsequently most often released as SO_2 in the regeneration of absorbent. The SO_2 may be processed further to form sulfuric acid or elemental sulfur.

TABLE 3.4-2. RANGE OF CONCENTRATIONS OF CHEMICAL CONSTITUENTS IN FGD SLUDGES FROM LIME, LIMESTONE, AND DOUBLE-ALKALI SYSTEMS[6]

Scrubber constituent	Sludge concentration range	
	Liquor, mg/liter (except pH)[a]	Solid, mg/kg[b]
Aluminum	0.03 - 2.0	
Arsenic	<0.004 - 1.8	0.6 - 52
Beryllium	<0.002 - 0.18	0.05 - 6
Cadmium	0.004 - 0.11	0.08 - 4
Calcium	180 - 2600	105,000 - 268,000
Chromium	0.015 - 0.5	10 - 250
Copper	<0.002 - 0.56	8 - 76
Lead	0.01 - 0.52	0.23 - 21
Magnesium	4.0 - 2750	
Mercury	0.0004 - 0.07	0.001 - 5
Potassium	5.9 - 100	
Selenium	<0.0006 - 2.7	2 - 17
Sodium	10.0 - 29,000	48,000
Zinc	0.01 - 0.59	45 - 430
Chloride	420 - 33,000	9,000
Fluoride	0.6 - 58	
Sulfate	600 - 35,000	35,000 - 473,000
Sulfite	0.9 - 3500	1600 - 302,000
Chemical oxygen demand	<1 - 390	
Total dissolved solids	2800 - 92,500	
pH	4.3 - 12.7	

[a] Liquor analyses were conducted on 13 samples from seven power plants burning eastern or western coal and using lime, limestone, or double-alkali absorbents.

[b] Solids analyses were conducted on six samples from six power plants burning eastern or western coal and using lime, limestone, or double-alkali scrubbing processes.

3.4.4 Energy Impacts

The increasing demand for energy in the United States is projected to be met in part by a significant increase in fossil fuel combustion. Energy consumption associated with FGD systems can vary widely with the process and vendor. Energy is required to run the recirculation and transfer pumps, booster fans, and other process equipment. Different processes also require varying degrees of energy use for absorbent makeup, absorbent regeneration (if required), and/or sludge disposal. Additional energy is consumed by use of fuel or steam to reheat flue gases and process steam in some of the regenerable FGD systems. This energy consumption can be provided by additional power generation. If the source does not produce power or if maximum power generation occurs, additional energy may have to be purchased; or the power boiler may be derated. Additional SO_2 emissions would be generated while producing the energy needed to operate the SO_2 control equipment.

3.4.4.1 Emission System Capacity Penalties--

The FGD systems cause losses in net generation by a power plant that sometimes requires the addition of generation capacity. The additional power-generating capacity required to compensate for the power used by the emission control system is a capacity penalty. These penalties can be expressed both as a percentage of the generating capacity of the unit controlled and as an additional operating cost in mills/kWh.

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3.5 THE SULFUR MARKET

Air pollution control regulations require the limitation of sulfur oxide emissions from combustion and industrial sources. The recovery of useful sulfur products from these emissions could help conserve natural resources and avoid the waste disposal problems often associated with nonregenerable SO_2 removal systems. Many factors affect the marketability of such products. Current data suggest that significant amounts of sulfuric acid could be produced from the SO_2 in power plant flue gas and sold in competitive markets.[1]

3.5.1 Types of Product

Sulfuric acid (H_2SO_4) is relatively simple to manufacture and at present is the most economically attractive product of SO_x abatement.[1] Although more complex to produce, elemental sulfur offers several marketing advantages over sulfuric acid and could become economically competitive.[2] The quality of elemental sulfur and sulfuric acid is important to their marketability.[3] The economic feasibility of other possible SO_x abatement products, such as liquid SO_2, liquid SO_3, and oleum (SO_3 dissolved in H_2SO_4), has not been seriously studied.

3.5.1.1 Sulfuric Acid--

Sulfuric acid is the most widely used industrial process chemical in the world.[4] Its production has been used as an indicator of general economic activity. High shipping costs and economies of production scale have led to concentrations of sulfuric acid manufacturers in certain areas.[4]

The quality and concentration of the sulfuric acid influence its marketability. Several items that can affect the resulting sulfuric acid are SO_2 concentration, particulate loading, water content, and contaminants in the incoming gas stream. Processes that yield a concentrated SO_2 stream for sulfuric acid manufacture are preferable to those that do not. For the protection of the vanadium pentoxide catalyst, particulate matter must be removed from the gas stream; in many cases other than when sulfur is burned to produce SO_2, the water is removed from the process gas stream. Another concern is condensed moisture in the acid. Most commercial sulfuric acid produced contains almost no dust and not more than 7 percent water.[5] The most common grades of sulfuric acid produced are 93 percent (66° Baumé) and 98 percent concentration.

3.5.1.2 Elemental Sulfur--

Elemental sulfur does not possess the hazardous, corrosive properties of sulfuric acid. It can be stored and shipped more easily than sulfuric acid and has a wider potential market in some areas.[6] The cost of the reducing agent [such as methane (natural gas), hydrogen sulfide, etc.], however, is often significant, and the reduction of SO_2 to elemental sulfur requires a relatively complex plant. The Claus process is widely used to produce elemental sulfur, especially in the petroleum and natural gas industries. There are two sulfur recovery units on utility FGD systems.

The color and purity of the sulfur product affect salability. A product with a color different from or purity less than that of Frasch sulfur would probably have to be priced lower.[7] The Frasch process is the method by which most of the virgin sulfur used in the United States is mined.

3.5.2 Industry Description

3.5.2.1 Sulfuric Acid--

The current annual production capacity of all manufacturers of virgin acid in the United States is 37.92 Tg (41,796,000 tons).[4] In addition, nonferrous smelters can produce 6.17 Tg (6,797,100 tons) per year of sulfuric acid.[4] Thus, the present total capacity is 44.08 Tg (48,593,100 tons) per year.[4] Tables 3.5-1 and 3.5-2 list the annual capacities of individual producers of virgin acid and smelter acid, respectively.

The yearly demand for sulfuric acid has increased since 1975 and is expected to continue to do so through 1985. Past, present, and future annual demands are summarized below:[4]

Year	Annual demand, Tg	(10^6 tons)
1975	29.628	(32.660)
1978	36.299	(40.013)
1979	37.533	(41.374)
1980	38.811	(42.782)
1983	42.906	(47.295)
1985	45.871	(50.565)

Sulfuric acid production increased at an annual rate of 3.4 percent from 1968 through 1978.[4] This growth rate is expected to continue through 1983.[4]

TABLE 3.5-1. ANNUAL CAPACITIES OF ALL U.S. PRODUCERS OF VIRGIN ACID IN 1979[4]

Producer	Annual capacity, Tg (tons)
Agrico Chemical, South Pierce, Fla.; Donaldsonville, La.	2.177 (2,400,000)
Allied Chemical, Anacortes, Wash.; Baton Rouge, Geismar, La; Buffalo, N.Y.; Chicago, Ill; Claymont, Del.; Elizabeth, N.J.; Fort Royal, Hopewell, Va.; Newell, Pa.; Nitro, W. Va.; Pittsburg, Richmond, Calif.	2.297 (2,532,000)
American Cyanamid, Joliet, Ill.; Linden, N.J.; New Orleans, La; Savannah, Ga.	1.039 (1,145,000)
Beker Industries, Conda, Idaho; Hahnville, La.; Marseilles, Ill.	1.429 (1,575,000)
Borden, Chesapeake, Va.; Piney Point, Fla.; Streator, Ill.	0.581 (640,000)
CF Industries, Bartow, Plant City, Fla.	3.112 (3,430,000)
Chevron, El Segundo, Calif.; Honolulu, Hawaii	0.120 (132,000)
Cities Service, Augusta, Ga.; Lake Charles, La.; Monmouth Junction, N.J.	0.286 (315,000)
Coulton Chemical, Oregon, Ohio	0.163 (180,000)
DuPont, LaPorte, Tex; Burnside, La.; Cleveland, North Bend, Ohio; Deepwater, Gibbstown, Linden, N.J.; East Chicago, Ind.; Richmond, Va.; Wurtland, Ky.	2.218 (2,445,000)
Essex Chemical, Newark, N.J.	0.163 (180,000)
Farmland, Industries, Green Bay, Fla.	1.138 (1,254,000)
First Mississippi, Fort Madison, Iowa	0.501 (552,000)
Freeport Minerals, Port Sulphur, Uncle Sam, La.	2.083 (2,296,000)
W.R. Grace, Bartow, Fla.	0.756 (833,000)
IMC, New Wales, Fla.	1.823 (2,010,000)
Kerr-McGee Nuclear, Grants, N. Mex.	0.127 (140,000)
LJ&M La Place Company, Edison, N.J.	0.091 (100,000)
Mississippi Chemical, Pascagoula, Miss.	0.907 (1,000,000)
Mobil Chemical, Depue, Ill.	0.363 (400,000)
Monsanto, Avon, Calif.; El Dorado, Ark.; Everett, Mass.; Sauget, Ill.	0.529 (583,000)
USI, DeSoto, Kan.; DeBuque, La.; Tuscola, Ill.	0.317 (349,000)
NL Industries, Sayerville, N.J.	0.544 (600,000)
Northeast Chemical, Wilmington, N.C.	0.109 (120,000)
Occidental Chemical, White Springs, Fla.; Plainview, Tex.; Lothorp, Calif.	1.981 (2,184,000)
Olin, Beaumont, Pasadena, Tex.; Curtis Bay, Md.; North Little Rock, Ark.; Shreveport, La.	1.173 (1,293,000)
Ozark-Mahoning, Tulsa, Okla.	0.091 (100,000)
Phelps-Dodge, Jeffrey City, Riverton, Wyo.	0.100 (110,000)
Philipp Brothers, Nichols, Fla.	0.408 (450,000)
US Phosphoric Products, Tampa, Fla.	1.814 (2,000,000)
Rohm and Haas, Deer Park, Tex.	0.640 (705,000)
Royster Company, Mulberry, Fla.	0.345 (380,000)
Swift, Bartow, Fla.; Calumet City, Ill.; Dothan, Ala.	0.243 (268,000)
J.R. Simplot, Pocatello, Idaho	0.581 (640,000)
Stauffer, Baton Rouge, La.; Baytown, Fort Worth, Manchester, Pasadena, Tex.; Dominguez, Martinez, Calif.; Hammond, Ind.; Le Moyne, Ala.	3.454 (3,807,000)
Texasgulf, Aurora, N.C.	1.880 (2,072,000)
Union Chemicals, Wilmington, Calif.	0.145 (160,000)
USS Agri-Chemicals, Bartow, Fort Meade, Fla.; Wilmington, N.C.	0.807 (890,000)
Valley Nitrogen Producers, Helm, Calif.	0.544 (600,000)
All others	0.840 (926,000)
Total	37.919 (41,796,000)

TABLE 3.5-2. ANNUAL CAPACITIES OF ALL U.S. PRODUCERS OF SMELTER ACID IN 1979[4]

Producer	Annual capacity, Tg (tons)
Amax Lead, Boss, Mo.	0.054 (60,000)
Amax Zinc Sauget, Ill.	0.113 (125,000)
Anaconda, Anaconda, Mont.	0.210 (231,000)
Asarco, Columbus, Ohio; Corpus Christi, El Paso, Tex.; East Helena, Mont.; Hayden, Ariz.; Tacoma, Wash.	0.670 (739,000)
Bunker Hill, Kellogg, Idaho	0.226 (249,000)
Cities Service, Copperhill, Tenn.	1.143 (1,260,000)
Climax Molybdenum, Fort Madison, Iowa; Langeloth, Pa.	0.179 (197,100)
Inspiration Consolidated Copper, Inspiration, Ariz.	0.397 (438,000)
Jersey Minere, Clarksville, Tenn.	0.118 (130,000)
Kennecott, Hayden, Ariz.; Hurley, N.Mex.; Salt Lake City, Utah	0.925 (1,020,000)
Magna Copper, San Manuel, Ariz.	0.397 (438,000)
National Zinc, Bartlesville, Okla.	0.082 (90,000)
New Jersey Zinc, Palmerton, Pa.	0.123 (136,000)
Phelps Dodge, Ajo, Morenci, Ariz,; Hidalgo, N. Mex.	1.159 (1,278,000)
St. Joe Minerals, Herculaneum, Mo.; Monaca, Pa.	0.368 (406,000)
Total	6.164 (6,797,100)

The price of sulfuric acid can vary enormously. Current published prices for virgin acid are $58.16 to $61.46 per Mg ($52.75 to $55.75 per ton) on the Gulf Coast, $61.36 to $64.66 per Mg ($55.65 to $58.65 per ton) in the Midwest, $63.73 to $67.03 per Mg ($57.80 to $60.80 per ton) on the West Coast, and $65.60 per Mg ($59.50 per ton) in the Northeast.[4] Smelter acid, however, can be purchased more economically from copper, lead, and zinc mining operations, mainly in the intermountain region and on the Gulf Coast. For smelter producers with little storage capacity on site, the necessity of disposing of acid can override other factors. Smelter producers state that the prices paid for smelter acid have been $15.44 to $19.85 per Mg ($14 to $18 per ton) on the Gulf Coast and $6.61 to $19.85 per Mg ($6 to $18 per ton) in the West.[4] Transactions are even reported at as low as $2.21 per Mg ($2 per ton).[4]

Sulfuric acid is used in many ways, although primarily for fertilizers. These uses are listed below:[4]

Use	Percentage of acid produced
Fertilizers	60
Petroleum refining	5
Copper leaching	5
Titanium dioxide	3
Hydrofluoric acid	2
Alcohols	2
Explosives	2
Aluminum sulfate	2
Ammonium sulfate	2
Iron and steel pickling	2
Cellulosics	1
Uranium milling	1
Surface active agents	1
Other	12
Total	100

The outlook for the sulfuric acid industry depends on many factors. Producers of virgin acid are in a cost/price squeeze: they face increased costs for Frasch and recovered sulfur (the main raw material in acid production), but must lower prices to compete with producers of inexpensive smelter acid. If recovered, all the SO_2 emissions from utilities and smelters could supply over 40.8 Tg (45 million tons) of sulfuric acid each year.[4] The economic feasibility of recovering significant amounts of sul-

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furic acid from power plants is restricted at present, but is expected to improve greatly by the end of the century.[4] Smelter acid will probably continue to keep prices down. Some anticipate that most smelter acid will be used for metallic ore leaching, whereas others anticipate that technological developments in leaching will make more smelter acid available for sale on the open market. Producers of virgin acid tend to claim that mining operations produce acid only to comply with pollution control regulations and warn that buyers of smelter acid are subject to the vagaries of the copper, lead, and zinc markets.[4] Domestic producers of virgin acid also face intense competition from Canadian Industries, Ltd., and as the Canadian government places more stringent limits on SO_2 emissions from metallic ore mining, smelter acid from Canada is likely to become a stronger factor in the U.S. market.[4]

3.5.2.2 Elemental Sulfur--

Elemental sulfur is produced by mining via the Frasch process and by recovery from sulfur-bearing gas streams (sour gas). In 1974, U.S. firms produced 10.7 Tg (10.5 million long tons) of elemental sulfur.[8] Sulfur mined by the Frasch process accounted for 74 percent of the total, sulfur recovered by the Claus process from sour gas amounted to roughly 20 percent of the total, and sulfur obtained as byproduct sulfur and from pyrite and other sources supplied the remaining 6 percent.[8]

Table 3.5-3 shows the annual capacities of the major U.S. producers of Frasch sulfur in 1973. Two of the 13 Frasch sulfur mines in 1973 were on anhydrite deposits, and 11 were on sulfur domes.[9] All the mines and sulfur processing firms were in Texas and Louisiana. Freeport Sulfur Co. and Texas Gulf Sulfur Co. together supplied about 60 percent of the total U.S. capacity to produce Frasch sulfur in 1973.[9]

Recovered sulfur in 1973 was produced by 132 plants, of which 64 recovered sulfur from refineries, 61 from natural gas sweetening operations, 4 from coke ovens, and 3 from other sources.[9] The plants were located in 23 states.[9] About 40 percent of them were in Texas, and most were relatively small.[9] Table 3.5-4 lists the annual capacities of the five largest U.S. producers of recovered sulfur in 1973.

The price of sulfur has varied widely during recent decades because of successive periods of shortage and oversupply.[10] The market could absorb

TABLE 3.5-3. ANNUAL CAPACITIES OF MAJOR U.S. PRODUCERS OF FRASCH SULFUR IN 1973[11]

Producer	Annual capacity, 10 Tg (long tons)
Arco Chemical, Fort Stockton, Tex.	0.183 (180,000)
Duval, Culberson County, Tex.	2.540 (2,500,000)
Freeport, Garden Island, La.	0.813 (800,000)
Freeport, Grand Ecaille, La.	1.422 (1,400,000)
Freeport, Grand Isle, La.	1.524 (1,500,000)
Freeport, Lake Pelto, La.	0.610 (600,000)
Jefferson Lake, Long Point, Tex.	0.305 (300,000)
Pan American Petroleum, High Island, Tex.	0.051 (50,000)
Texas Gulf, Bullycamp, La.	0.305 (300,000)
Texas Gulf, Fannett, Tex.	0.178 (175,000)
Texas Gulf, Moss Bluff, Tex.	0.305 (300,000)
Texas Gulf, Newgulf, Tex.	1.524 (1,500,000)
Texas Gulf, Spindletop, Tex.	0.686 (675,000)
Total	10.446 (10,280,000)

TABLE 3.5-4. ANNUAL CAPACITIES OF THE FIVE LARGEST U.S. PRODUCERS OF RECOVERED SULFUR IN 1973[11]

Producer	Annual capacity, Tg (long tons)
Exxon Company	0.260 (256,000)
Getty Oil Company	0.231 (227,000)
Shell Oil Company	1.077 (1,060,000)
Standard Oil Company of California	0.165 (162,000)
Standard Oil Company of Indiana	0.464 (457,000)
Total	2.197 (2,162,000)

large quantities of sulfur with little decline in price during shortages.[10] In times of oversupply, however, the production of large quantities of sulfur from SO_x abatement could force prices down.

The future of the sulfur market depends considerably on the supplies of sulfur produced by mining and by recovery from sour gas. Mining reserves appear to be declining and may be exhausted within 20 or 30 years.[10] Reports indicate that old reserves are being depleted faster than new reserves are being found and that costs are increasing as less accessible reserves of lower quality are mined.[10] The amount of sulfur recovered from sour gas is increasing in several countries, especially Canada.[10] Such byproduct or coproduct sulfur is recovered independently of market demand and thus tends to depress prices.

3.5.3 Plant Location

Plant location is an important factor in the sale of sulfur products from SO_x abatement. The large quantities of such products that could come from a power plant require making large sales to single customers, selling through an established marketer of sulfur products, or incurring high marketing costs. Phosphate fertilizer plants are the dominant consumers of sulfur products in the United States and are large enough to provide the individual points of high consumption for SO_x abatement products. For example, a fertilizer plant producing 1 Tg (1100 tons) per day of phosphate fertilizer (i.e., a plant in the current upper size range) uses 2.80 Tg (3080 tons) per day of sulfuric acid, the possible output from 3000 MW of power generating capacity.[12]

If high transportation costs are to be avoided, the phosphate fertilizer plant should be fairly close to the power plant. Most fertilizer plants, however, are on the Gulf Coast, an area of relatively little power generation.[13] Much SO_x is emitted in the Northeast, where little fertilizer is produced.[14] Fertilizer and power production are nearly balanced in the East North Central region.[14] Phosphate fertilizer is heavily consumed in the upper Midwest, where about 90 percent of all coal with a sulfur content of more than 3.5 percent is mined.[14] Recovery economics tend to be less favorable in the East because, in general, the coal mined there contains less sulfur.[14] The low cost of barge shipment may make the long-distance transportation of SO_x abatement products economically feasible from power plants on or near navigable waters.[14]

3.5.4 Outlook for SO_x Abatement Products

The EPA has sponsored a study by the Tennessee Valley Authority (TVA) to evaluate the market potential for sulfuric acid and elemental sulfur from SO_x abatement. The TVA has developed a cost model to determine the least expensive method for power plants to comply with air pollution control regulations. Three methods of compliance have been considered: (1) burning a clean fuel, (2) scrubbing with a nonregenerable limestone FGD system, and (3) scrubbing with an FGD system that includes the recovery of sulfuric acid or elemental sulfur. The TVA has investigated the distribution of SO_x abatement products in competition with existing producers for power plants where the production of SO_x abatement products appears economically feasible. These investigations indicate that significant amounts of sulfuric acid could be recovered from power plant flue gas and sold in competitive markets.[15]

In determining the least expensive strategy for compliance with air quality regulations, the TVA has devoted much attention to the clean fuel alternative, which is defined as the increased price that a power plant would pay for low-sulfur fuel to meet applicable regulations concerning SO_2 emissions.[16] Several price increases have been considered for several increments of heat input.*

The TVA suggests that large new power plants with high load factors are most likely to find recovery of sulfur products economically attractive. The boilers of the best candidate plants are usually less than 10 years old.[17] The average size is about 600 MW, and the average capacity factor is about 60 percent.[17]

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* This study uses the International System of Units (SI). Boiler capacities are expressed in watts thermal, the SI units for power. The available data about boilers are given in English units and have been converted to SI values.

† Equivalent to $0.50 in mid-1983 dollars.

3.5.4.1 Sulfuric Acid--

The TVA projected that 94 power plants with 165 boilers will be out of compliance with air pollution control regulations in 1983.[18] Sulfuric acid production in 1983 was considered for five of these plants at an additional clean fuel cost of $1.30 (in mid-1979 dollars) per MW thermal ($0.38 per million Btu/h†) and for 26 plants at an additional clean fuel cost of $1.81 (in mid-1979 dollars) per MW thermal ($0.53 per million Btu/h*).[18] Detailed analysis was limited to the latter situation, in which the combined annual capacity of the 26 power plants to produce sulfuric acid would exceed 4.17 Tg (4,600,000 tons).[18] At only seven plants, however, is a market potential in 1983 anticipated. The sales from these seven plants would total 1.128 Tg (1,243,000 tons) in 1983, if the additional clean fuel cost is $1.81 (in mid-1979 dollars) per MW thermal ($0.53 per million Btu/h*).[6]

3.5.4.2 Elemental Sulfur--

The TVA data for 1978 and 1983 show no sales of elemental sulfur from SO_x abatement systems.[19] Such FGD sulfur could, however, become competitive in some places with sulfur from Port Sulphur, Louisiana, if the total costs of producing FGD sulfur were reduced by relatively small amounts. The cost of producing FGD sulfur at 16 power plants is expected to be relatively low in 1983.[19] Sulfur from one plant could become competitive with a reduction in total FGD sulfur production costs of 3.1 percent.[19] Sulfur from the other 15 plants could become competitive with reductions ranging from 5.4 to 23.7 percent.[19] The annual production of the 16 plants would amount to 0.241 Tg (265,723 short tons or 237,252 long tons).[19]

Even if there are no economic reasons for producing recovered elemental sulfur, it may be desirable to produce elemental sulfur because of the ease of storage and disposal of sulfur as opposed to the problems of disposing of calcium-based sludge.

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[*] Equivalent to $0.70 in mid-1983 dollars.

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SECTION 4

COMBUSTION PROCESSES

4.1 NATURE AND EXTENT OF SULFUR OXIDE (SO_x) EMISSIONS FROM COMBUSTION

Combustion of fuels at stationary sources generates by far the greatest portion of total sulfur oxide (SO_x) emissions nationwide, which was more than 82 percent in 1977.[1] This section deals with the combustion processes that make up this important category of sulfur oxide sources. A brief overview is presented, followed by a detailed discussion of currently available technology for the control of SO_x emissions from combustion processes, as well as the technology that is anticipated or under development.

Stationary combustion sources consist of electric utilities and industrial, residential, commercial, and institutional sources. Figure 4.1-1[2] shows the total estimated SO_x emissions nationwide and the portion due to stationary sources in the period from 1970 through 1977. This figure shows a slight decrease (9 percent) in total SO_x emissions during the period. Although the SO_x emissions from stationary fuel combustion sources also decreased slightly (1 percent) over the same period, these sources represent an increasingly greater portion of the U.S. total. This increase can be attributed to the electric utility industry, which is estimated to have been responsible for more than 64 percent of the total SO_x emissions in 1977 as compared with 53 percent in 1970.[3]

Coal burning by utilities contributes greatly to the increase. Given equivalent sulfur contents, coal firing would release almost 1.5 times the amount of SO_x released in oil firing to generate the same amount of heat. In 1977 coal-fired power plants represented 37 percent of all the electric generating capacity in the United States[4] and were responsible for almost 92 percent of the utility SO_x emissions.[5] Oil firing accounted for the remainder.

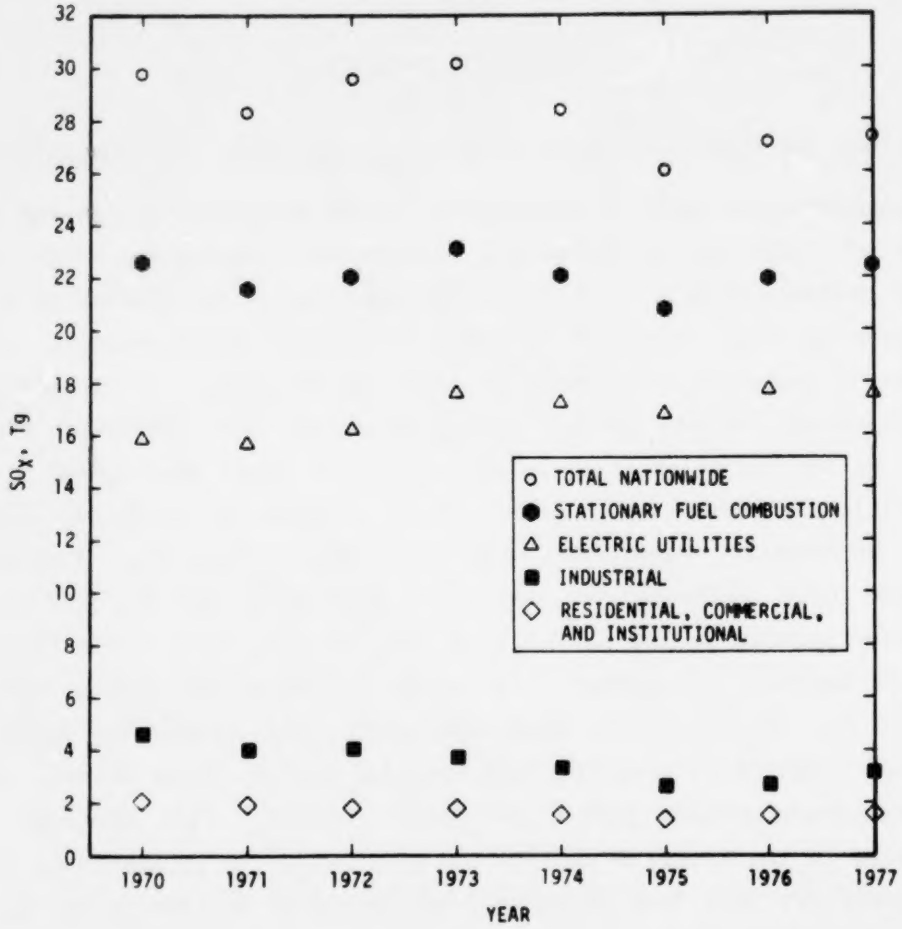

Figure 4.1-1. Nationwide SO_x emission estimates.[2]

Projections are that the use of electricity will increase, although possibly at a lower annual rate because of energy conservation measures and a lower rate of population growth. In 1979, 39 percent of the electric generating capacity in the United States was from coal; the percentage of electric generating capacity from coal is expected to be 41 percent by 1990.[6] According to the National Coal Association, over 250 coal-fired plants are being planned or under construction for the 10-year period 1978-1987.[7] Utility coal consumption will increase correspondingly from 433 teragrams (477.5 million tons) in 1977[8] to more than 635 teragrams (700 million tons) by 1985.[9] Although not as dramatic as the increase in usage by electric utilities, the industrial use of coal is also projected to increase and to reach 96.2 teragrams (106 million tons) by 1985.[9]

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4.2 CONTROL TECHNIQUES

Various methods of reducing sulfur oxide (SO_x) emissions from combustion sources are either available or under development. These control methods can be grouped into four major categories: 1) fuel substitution, 2) fuel desulfurization, 3) flue gas desulfurization, and 4) combustion process modifications. Economics and/or status of technological development are major determinants in the selection of an SO_x control technique.

4.2.1 Fuel Substitution

The most straightforward method of reducing SO_x emissions is to burn fuels that cause lower SO_x emissions than those now in use. This can involve either the switching of fuels in existing sources (i.e. low-sulfur coal or oil for high-sulfur coal) or the substitution of energy sources (i.e., hydropower for coal-fired power plants). Because of problems associated with the availability of cleaner fuels in the long term and because of energy legislation, the substitution of coal with oil or natural gas may no longer be an acceptable sulfur dioxide (SO_2) control technique.

4.2.1.1 Coal--

Coal is perhaps the only domestic fuel with which the United States can meet projected energy demands beyond the year 2000. The U.S. demonstrated coal reserve is estimated to be about 397 petagrams (438 billion tons). (See Table 4.2-1.)[1] At a minimum recoverability of 50 percent and the 1976 domestic consumption rate of 535 teragrams per year (590 million tons per year),[2] the domestic coal supply would last at least 370 years.

The United States has large reserves of low-sulfur (less than 1 percent) coal predominantly in the western states. (See Table 4.2-2.)[3] It is estimated[4] that 99.79 petagrams (110 billion tons) of recoverable coal could be fired as is, in compliance with the previous New Source Performance Standard (NSPS) of 520 nanograms per joule heat input (1.2 pounds SO_2 per million Btu heat input). A more stringent SO_2 emission standard would reduce the amount of compliance coal available, as shown in Table 4.2-3.[5]

Initially, firing of low-sulfur western coal appears to be an ideal method of reducing SO_x emissions; several considerations, however, limit the widespread adoption of low-sulfur coal firing. Much of the low-sulfur coal

TABLE 4.2-1. DEMONSTRATED COAL RESERVE BASE BY RANK AND POTENTIAL METHOD OF MINING, JANUARY 1, 1976[1]
Pg (Billion Short Tons)

Mining method and area	Anthracite	Bituminous	Sub-bituminous	Lignite	Total[a]
Underground					
East of Mississippi River	6.35 (7)	140.62 (155)	0	0	146.97 (162)
West of Mississippi River	b	24.49 (27)	97.98 (108)	0	122.47 (135)
Total underground	6.35 (7)	165.11 (182)	97.98 (108)	0	269.44 (297)
Surface					
East of Mississippi River	b	35.38 (39)	0	0.91 (1)	37.20 (41)
West of Mississippi River	b	7.26 (8)	55.34 (61)	29.94 (33)	91.63 (101)
Total surface	b	42.64 (47)	55.34 (61)	30.85 (34)	127.92 (141)
Grand total[b]	6.35 (7)	207.75 (229)	153.32 (168)	30.85 (34)	397.35 (438)

[a] Sum of components may not equal total because of independent rounding.

[b] Less than 0.45 Pg (0.5 billion short tons).

Note: Includes measured and indicated categories as defined by the Bureau of Mines and U.S. Geological Survey and represents 100 percent of the coal in place. Recoverability varies between 40 and 90 percent for individual deposits. Fifty percent or more of the overall coal reserve base in the United States is estimated to be recoverable.

Source: Bureau of Mines.

TABLE 4.2-2. DEMONSTRATED COAL RESERVE BASE BY SULFUR CONTENT AND POTENTIAL METHOD OF MINING, JANUARY 1, 1976[3]
Pg (Billion Short Tons)

Mining method and area	<1%	Sulfur range 1.1-3%	>3%	Unknown	Total
Underground:					
East of the Mississippi River	23.59 (26)	42.64 (47)	58.06 (64)	23.59 (26)	146.97 (162)
West of Mississippi River	92.53 (102)	9.98 (11)	7.26 (8)	12.70 (14)	122.47 (135)
Total underground	114.31 (126)	52.62 (58)	66.23 (73)	35.38 (39)	269.44 (297)
Surface:					
East of Mississippi River	6.35 (7)	7.26 (8)	17.24 (19)	6.35 (7)	37.20 (41)
West of Mississippi River	59.88 (66)	23.59 (26)	2.72 (3)	4.54 (5)	91.63 (101)
Total surface	68.95 (76)	30.84 (34)	18.14 (20)	9.98 (11)	127.92 (141)
Grand total	182.35 (201)	84.37 (93)	84.37 (93)	46.27 (51)	397.35 (438)

Note: Data may not add to totals shown because of rounding. Includes measured and indicated categories as defined by the Bureau of Mines and Geological Survey, and represents 100 percent of the coal in place. Recoverability varies between 40 and 90 percent for individual deposits. Fifty percent or more of the overall coal reserve base in the United States is estimated to be recoverable.

Source: Bureau of Mines.

TABLE 4.2-3. ESTIMATES OF RECOVERABLE RESERVES OF RAW COAL CHARACTERIZED BY SO_2 EMISSION RATE FROM UNCONTROLLED COMBUSTION[5]

Region	Recoverable reserve Pg (millions of tons)	SO_2 emission rate, ng/J (lb/10^6 Btu)							
		520 (1.2)		340 (0.8)		260 (0.6)		170 (0.4)	
		% of Reserve	Gg, (millions of tons)	% of Reserve	Gg, (millions of tons)	% of Reserve	Gg, (millions of tons)	% of Reserve	Gg, (millions of tons)
Eastern	52.6 (58,000)	12	6.4 (7,000)	2	1.1 (1,200)	<1	0 0	0	0 0
Eastern Midwest	46.3 (51,000)	1	0.5 (510)	0	0 0	0	0 0	0	0 0
Western Midwest	11.8 (13,000)	5	0.6 (650)	2	0.2 (260)	0	0 0	0	0 0
Western	127.0 (140,000)	70	88.9 (98,000)	41	51.7 (57,000)	16	20.0 (22,000)	2	2.5 (2,800)
Total U.S.	237.7 (262,000)	42	96.3 (110,000)	22	53.0 (58,000)	8.4	20.0 (22,000)	1.1	2.5 (2,800)

available in the East is coking coal used primarily by the steel industry. Capacity for mining and production of eastern low-sulfur coal is also limited. Further, the vast reserves of low-sulfur western coal must be transported over long distances for use by the majority of the coal-burning plants, which are located in the East and Midwest. Facilities for transportation from western mines to eastern markets may be inadequate. Apart from the transportation problem, firing of low-sulfur western coal in boilers not originally designed for it is limited by the need for substantial boiler modifications or boiler derating.[6] Finally, because the heat content of western coal is generally lower, more western coal is often needed to generate the same amount of power as eastern coal.[7] Table 4.2-4[7] gives data on eastern and western coal firing.

4.2.1.2 Oil--

Residual and distillate oil accounted for approximately 21 percent[8] of the electricity generated by utilities in 1977 and almost 28 percent[9] of the energy consumed by industrial/commercial boilers in 1975. At one time, national policies directed toward reducing SO_x emissions prompted operators to convert their boilers from coal to oil firing. In light of recent developments in the international oil markets, this method of reducing emissions is no longer practicable.

Figures 4.2-1[10] and 4.2-2[10] show world production of crude oil and daily demand in 1976. The U.S. dependence upon foreign producers to meet demand is obvious. In 1977 the U.S. portion of crude oil production dropped to 14 percent[11] of the total production worldwide.

In 1976 the United States imported about 40 percent of all its petroleum. Current U.S. policies aimed at reducing dependence on foreign oil virtually eliminate the substitution of oil as an SO_x control technique.

4.2.1.3 Natural Gas--

Twenty-seven percent of all U.S. energy consumption in 1976 was provided by natural gas. Domestic production accounted for about 95 percent of consumption.[12] If sufficient quantities were available, substituting natural gas for coal and oil could lead to large reductions of SO_x emissions; however, the proved reserves of natural gas peaked around 1970 and

TABLE 4.2-4. SO_2 EMISSIONS FROM BURNING DIFFERENT COALS[a,7]

% sulfur in coal	Heat basis, ng/J (lb $SO_2/10^6$ Btu)		Electrical generation 1000 MWe plant,[b] Gg/yr (tons SO_2/yr)	
	Western coal at 20,880 J/g (9000 Btu/lb)[c]	Eastern coal at 30,160 J/g (13,000 Btu/lb)[d]	Western coal at 20,880 J/g (9000 Btu/lb)[c]	Eastern coal at 30,160 J/g (13,000 Btu/lb)[d]
0.2	170 (0.4)	130 (0.3)	12.7 (14,000)	9.1 (10,000)
0.6	560 (1.3)[e]	390 (0.9)	39.9 (44,000)[e]	27.2 (30,000)
1.0	900 (2.1)[e]	650 (1.5)[e]	64.4 (71,000)[e]	45.4 (50,000)[e]
3.0	2700 (6.3)[e]	1890 (4.4)[e]	190.5 (210,000)[e]	136.1 (150,000)[e]
5.0	4560 (10.6)[e]	3140 (7.3)[e]	326.6 (360,000)[e]	226.8 (250,000)[e]
7.0	6360 (14.8)[e]	4390 (10.2)[e]	453.6 (500,000)[e]	308.4 (340,000)[e]

[a] Based on 5% sulfur residue in ash.

[b] Basis: No SO_2 controls, 75% operating time, 33% thermal efficiency, 71.0×10^{15} J/yr (67.3×10^{12} Btu/yr) thermal input.

[c] Typical of high-ash western coals with 0.2 to 3.0 percent sulfur.

[d] Typical of high-quality eastern steam coals.

[e] Does not meet EPA standard: 520 ng/J (1.2 lb $SO_2/10^6$ Btu).

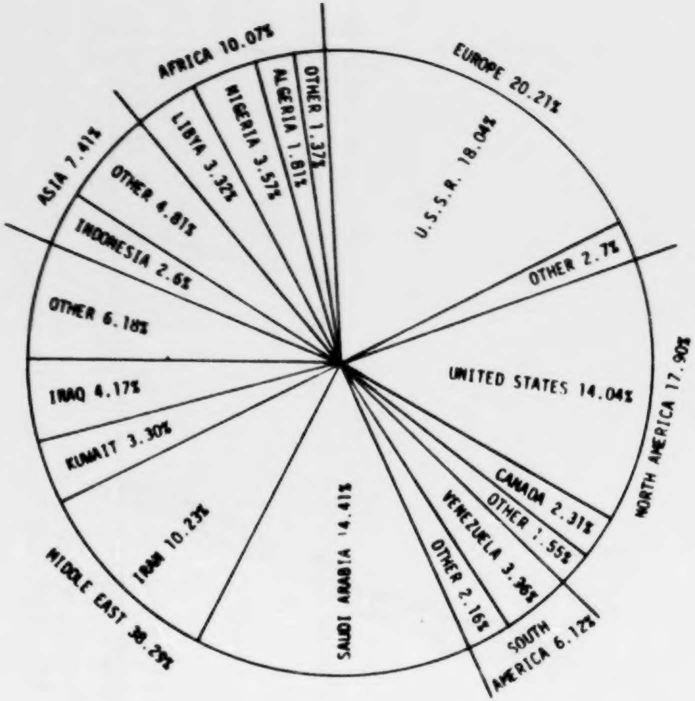

Figure 4.2-1. World share of crude oil production, in 1976.[10]

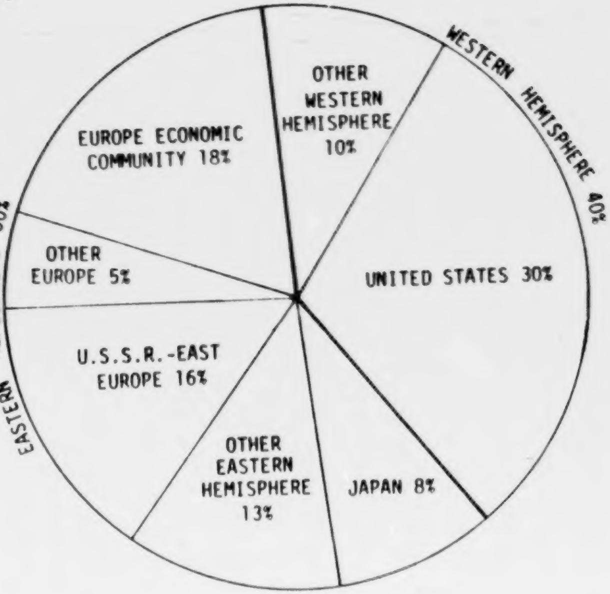

Figure 4.2-2. World daily petroleum demand, 1976.[10]

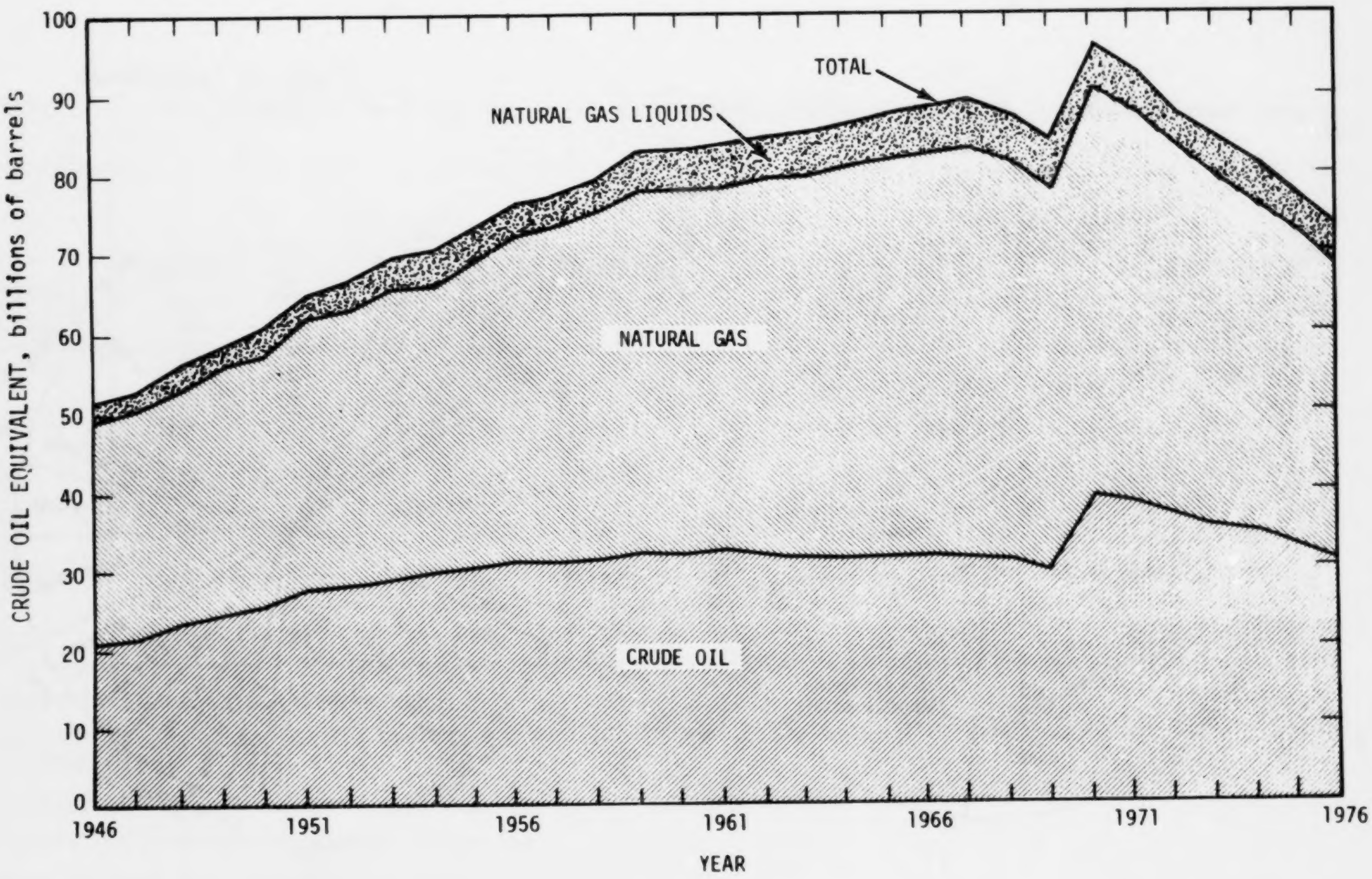

Figure 4.2-3. Proved reserves of liquid and gaseous hydrocarbons, year-end 1976.[13]

have been declining since that time, as shown in Figure 4.2-3.[13] Because of gas curtailments and declining production, projections indicate a slightly increasing demand in the residential and commercial sectors and a reduction in industrial and utility use. This will probably result in higher SO_x emissions because of the substitution by higher sulfur fuels.[14]

4.2.1.4 Source Substitution--

Other sources of energy that could alleviate SO_x emissions are nuclear power, hydroelectric power, and other possible power sources. Growth of nuclear power has fallen short of early projections. Although capacity is expected to increase, public concern for safety and environmental effects are constraining growth of this energy source. In any case the reduction of SO_x emissions due to increased utilization of nuclear power will probably be minimal, since it will be replacing the relatively clean but scarce fossil fuels--oil and natural gas--rather than coal.

The total quantity of hydropower is also expected to grow; its percentage of contribution to the total energy supply, however, will decrease. Thus, the increases in use of hydropower will lead to no substantial reductions in SO_x emissions.

The effects of other energy sources such as solar, geothermal, and wind power on the total energy supply will be minimal in the mid-term (1980's), as will be their contribution to reduction of SO_x levels. Extensive and rapid shifts in the current modes of power generation and energy use would be difficult and would entail a great technological development.

4.2.2 Fuel Desulfurization

Desulfurization of fuel prior to combustion, like fuel substitution, is a principal near-term solution to the SO_x emissions problem. Desulfurization of oil and natural gas has been practiced for some time; current technology can reduce the maximum sulfur content of residual oil to 0.5 percent and of natural gas to less than 0.1 percent. It is unlikely, however, that substantial reductions of total SO_x emissions can be achieved by oil or gas desulfurization, given the anticipated limitations on usage of these fuels. Cleaning or desulfurization of coal provides greater opportunities to reduce

SO_x emissions due to combustion. Processes yielding synthetic fuels, such as liquefaction and gasification of coal, are being developed primarily to provide substitutes for limited oil and natural gas resources; however, these processes also reduce SO_x emissions from combustion and are therefore considered here.

4.2.2.1 Coal Cleaning--

Physical and chemical coal cleaning processes are being developed specifically to provide cleaner fuels.

Physical coal cleaning--Sulfur occurs in coal primarily in one of two nonelemental forms, inorganic and organic. Organic sulfur is chemically bound to the coal substance. Inorganic sulfur occurs with iron as discrete particles of pyrite in the coal. Inorganic sulfur is amenable to physical coal cleaning, whereas the organic form is not.

Reducing the quantities of ash-forming impurities has been the primary function of physical coal cleaning. When some of the impurities are pyrites, the sulfur content of the coal is reduced simultaneously.[15] Up to 90 percent of the pyritic sulfur in coal can be eliminated by physical cleaning, yielding a total sulfur reduction of 10 to 40 percent.[16]

Physical coal cleaning processes generally involve crushing run-of-mine coal to a point where some of the mineral and coal particles are then separated by techniques usually based on differences in the densities or surface properties of the particles. The coal is then often dried. The maximum sulfur removal obtainable with most coals is about 40 percent.[17]

Most existing physical coal cleaning techniques depend upon differences in the density of coal and the impurities it contains.[18] Hydraulic jigs, hydroclones, concentrating tables, dense-medium vessels, and classifiers can separate ground coal from the more dense impurities.

In the use of hydraulic jigs, a pulsating fluid flow stratifies coal particles from top to bottom. The less dense cleaned coal overflows at the top. This is the most popular and the least expensive coal washer available; however, it may not give an accurate separation. It is used on coal ranging in size from 6 to 200 mm (¼ to 8 in.).[19]

In the use of hydroclones, the separating mechanism is located in the ascending vortex. The particles of various densities or specific gravities move upward in this current and are subjected to centrifugal forces that effect separation. For maximum reduction of pyrites and maximum yield of cleaned coal, supplemental processes are used such as screening and froth flotation. Hydroclones are most often used to clean flotation-sized coal, but they can be used for coal as coarse as 64 x 0 mm. (¼ x 0 in.).

When froth flotation is used, a coal slurry is mixed with a collector to make a certain fraction of the mixture hydrophilic. Normally this is the coal fraction although it may vary with ash physical properties and the collector used. A frother is added, and finely disseminated air bubbles are introduced into the mixture. Air-bubble-adhering particles of cleaned coal normally are floated to the top of the slurry and are removed by a skimming device. The froth is then broken, and the coal concentrate is recovered. Thus both density differences and the surface properties of the coal and ash are used to achieve separation. This is normally used with coal in the 1.17 to 0.044 mm (14 to 325 mesh) range.

Another common method of coal cleaning is the use of concentrating tables. A pulverized coal and water slurry is floated over a table, which is shaken with a reciprocating motion. The lighter coal is separated to the bottom of the table, while the heavier, larger particles containing most of the undesirable impurities move to the sides. These tables are normally used with coal in the 0.15 to 6.4 mm (100 mesh to ¼ in.) range.

For dense-medium vessels, a slurry of coal is prepared in a medium with a specific gravity close to that at which the separation is to be made. Lab tests on the coal determine at what density the desired amount of pyrites can be removed. The lighter, purer coal that floats to the top is continuously skimmed off. A major advantage of this system is that it allows a sharp separation at any specific gravity within the range normally required. Dense-medium vessels can handle coal in the 0.59 to 200 mm (28 mesh to 8 in.) range.

With pneumatic or air classification, coal and refuse particles are stratified through the action of pulsating air. The denser layer containing pyrites is collected in pockets or wells and is removed. The upper layer of cleaned coal travels over the denser refuse layer and is removed at the opposite end of the equipment. Air classification can be used with coal up to a particle size of 6.4 mm (¼ in.).

Other physical techniques that may be developed and become widespread are oil agglomeration, high-gradient magnetic separation, two-stage flotation, and use of fine-particle dense-medium cyclones.[20] Although it is well established, current technology cannot produce coal that can ensure compliance with SO_x emission regulations, and no major changes are expected before 1990.[21] Table 4.2-5 shows the potential for sulfur reduction by different degrees of physical coal cleaning.[22]

Chemical coal cleaning--Chemical coal cleaning methods are under development to increase the potential for sulfur removal over that offered by physical coal cleaning. Some chemical processes have claimed to remove more than 95 percent of the pyritic sulfur and about 70 percent of the organic sulfur.[23] Some 25 chemical coal cleaning methods are being actively developed, and others are in the conceptual development stage.[24] Because many of the processes are in the early development phases, it is estimated that achieving commercial operation will require at least 5 to 10 years.

Economics are expected to limit the amount of sulfur removed to 95 percent of the pyritic sulfur and about 40 percent of the organic sulfur.[23] Table 4.2-6 shows the potential for sulfur reduction by different degrees of chemical coal cleaning.[25]

Economic and environmental impacts--The mid-1979 capital cost of physical coal cleaning of northern Appalachian coals has been estimated for a 454 Mg (500 tons) per hour, mine-mouth coal cleaning facility as being between $11,500 and $57,500 per Mg ($10,400 to $52,100 per ton) per hour capacity. The mean cost range is $19,200 to $22,900 per Mg ($17,400 to $20,900 per ton) per hour capacity.

For this unit, the annual capital charges and operating and maintenance costs in mid-1979 dollars yielded a cleaned coal processing cost of $5.46 per Mg ($4.95 per ton) of cleaned coal. Other more detailed costs are shown in Table 4.2-7.

The cost estimated for chemical coal cleaning is more difficult since most of the systems are in the developmental or pilot stages and have not been demonstrated. Economic information (shown in Table 4.2-8) on eight of

TABLE 4.2-5. POTENTIAL FOR REDUCING EMISSIONS BY PHYSICAL DESULFURIZATION[a],22

	Average pyrite removed, %		Average reduction in SO_2 emissions, %		Average emission level on combustion, ng/J (lb $SO_2/10^6$ Btu)	
	Low[b]	High[c]	Low	High	Low	High
Uncleaned coal					470-860 (1.1-2.0)	2060-3870 (4.8-9.0)
Common commercial practice[d]	28-43	37-55	11-17	30-40	390-770 (0.9-1.8)	1290-2790 (3.0-6.5)
Best current commercial technology[e]	43-63	70-80	16-20	45-55	390-650 (0.9-1.5)	950-1890 (2.2-4.4)
Best potential technology[f]	90	90	30-45	50-60	340-470 (0.8-1.1)	820-1500 (1.9-3.5)

[a] Based on data from Bureau of Mines RI 8118 for coal averages from six coal regions.

[b] Low-sulfur coals from southern Appalachian, Alabama, and western coal regions.

[c] High-sulfur coals from northern Appalachian, eastern Midwest, and western Midwest regions.

[d] Crushed to 3.81 cm (1-1/2 inch) top size and separated at 1.6 SG.

[e] Crushed to 0.95 cm (3/8 inch) top size and separated at 1.3 SG. Sink fraction pulverized and upgraded to fire at higher emission level.

[f] Combination of crushing and physical separation techniques required to achieve 90 percent pyrite removal.

Note: It is convenient to group the average coal from each of the six coal regions into high and low groups because the percentage of pyrite that can be removed by gravimetric separation increases as the percentage of coal pyrite increases. Sulfur content and physical desulfurization potential of individual coals from each region differ significantly from the average "regional" values; the sulfur content of many uncleaned and desulfurized coals falls in the range between the low and high values.

TABLE 4.2-6. POTENTIAL FOR REDUCING EMISSIONS BY CHEMICAL DESULFURIZATION[a,25]

	Average sulfur removed,		Average reduction in SO_2 emissions, %		Average emission level on combustion, ng/J (lb $SO_2/10^6$ Btu)	
	Pyritic	Organic	Low[b]	High[c]	Low	High
Uncleaned coal					520-860 (1.2-2.0)	210-3870 (4.8-9.0)
Pyrite leaching[d]	95	0	32-50	56-65	340-430 (0.8-1.0)	770-1380 (1.8-3.2)
Best available technology[e]	95	25	48-62	66-73	260-340 (0.6-0.8)	600-1070 (1.4-2.5)
Best practical technology[f]	95	40	58-69	72-77	215-260 (0.5-0.6)	470-860 (1.1-2.0)

[a] **Based on data from Bureau of Mines RI 8118 for coal averages from six coal regions.**

[b] Low-sulfur coals from southern Appalachian, Alabama, and western coal regions.

[c] High-sulfur coals from northern Appalachian, eastern Midwest, and western Midwest regions.

[d] Meyers Process.

[e] ERDA/USBM or Battelle hydrothermal process.

[f] Undefined advanced process.

TABLE 4.2-7. SUMMARY OF PHYSICAL COAL CLEANING PLANT COSTS[26]

Process	Capacity, Mg/h (ton/h)		Capital costs, $ per Mg/h (ton/h)	Btu recovery, %	Annualized costs		
	Input	Output			Dollars per Mg (per ton) of raw coal	Dollars per Mg (per ton) of clean coal	Dollars per GJ (million Btu)
Jig-simple	544 (600)	321 (351)	7276 (6600)	91.6	2.17 (1.97)	3.69 (3.35)	0.131 (0.138)
Jig-intermediate	907 (1000)	647 (714)	15104 (13700)	96.4	2.91 (2.62)	4.04 (3.67)	0.144 (0.152)
Jig-intermediate	907 (1000)	513 (566)	13230 (12000)	83.0	2.45 (2.22)	4.31 (3.92)	0.149 (0.157)
Jig-complex	1451 (1600)	864 (953)	15766 (14300)	93.7	2.86 (2.60)	4.81 (4.36)	0.153 (0.162)
Dense medium-simple	1269 (1400)	939 (1036)	15435 (14000)	94.6	3.08 (2.79)	4.18 (3.76)	0.175 (0.185)
Dense medium-complex	544 (600)	396 (440)	24888 (22400)	89.2	3.93 (3.54)	5.36 (4.83)	0.168 (0.177)
Dense medium-complex	544 (600)	324 (360)	15555 (14000)	93.1	2.32 (2.09)	3.86 (3.48)	0.130 (0.137)
Dense medium-complex	810 (900)	696 (774)	25777 (23200)	94.3	3.23 (2.91)	3.75 (3.38)	0.128 (0.135)

TABLE 4.2-8. MAJOR COAL CLEANING PROCESS DATA[27]

Process	Plant size basis, Mg/h (tons/h)	Costs[a]			Sulfur removal		
		Capital, $10⁶	Processing,[b] $/Mg	($/ton)	Pyritic, %	Organic, %	Btu recovery, %
Physical[c]	454 (500)	10.4	5.46	(4.95)	35-70		80-95
TRW/Meyers[c]	345 (380)	168	13-18	(12-16)	95		90
Battelle Hydrothermal	363 (400)	155-168	23-32	(21-29)	99	24-72	75-90
Hazen	300 (330)	56	18	(16)	80		76
KVB	300 (330)	79	29	(27)	99	13	90
Ledgemont Oxygen Leaching	300 (330)	174	24	(22)	95		93
BOM/ERDA	300 (330)	151	24	(22)	99	15	94
Dynatech	300 (330)		5.17	(4.69)			
GE	363 (400)		8.43	(7.65)	50 combined		

[a] Costs are adjusted to mid-1979.

[b] Includes capital charge and operating and maintenance costs; basis for costs are cleaned coal.

[c] See Reference 28 for basis of costs and other data.

the processes is compared with that for physically cleaned coal in the 1978 report.

In addition to the economic considerations of coal cleaning, the environmental impact of these systems must be considered. Physical coal cleaning is normally achieved in mine-mouth facilities, and the process wastes are normally disposed of on site. Some major areas of concern in a physical coal cleaning facility are as follows:

- Operations causing major emissions of air pollutants are infrequent in physical coal cleaning. The largest air emissions are fugitive dust from coal handling, transfers, and size reduction in the grinding step and both particulate matter and combustion products from coal dryers.
- Water-related problems have essentially two sources: additives used in the physical coal cleaning cells that can be introduced to the outside environment as system purges or when cells are dumped and heavy metals and inorganic compounds that may be leached from the coal. Heavy metals are often introduced into aquatic ecosystems as byproducts of acid mine drainage. Heavy metals can be highly toxic and bioaccumulative. Work in this area is ongoing.
- The amount of coal solids that remains at a physical coal cleaning site depends on the raw coal properties and the degree of coal cleaning. Besides the problem of the sheer volume of solids to be disposed of, there are two concerns: fugitive dust problems and leaching of inorganic compounds and heavy metals from the solids. A study of the possible stabilization of coal preparation wastes is being performed.
- One other area of concern is the possibility of fire in reject coal piles. This is considered a mismanagement problem, rather than a process problem.

The environmental problems associated with chemical coal cleaning are less well identified because of the status of development of many of the processes. In general, however, there are particulate matter problems associated with coal handling, transfer, and size reduction, and there are particulate and at times solvent release problems associated with drying steps. The gas stream from some of the reactors can include carbon monoxide and nitrous oxides, which may present problems.

Solvent handling and the handling of various alkalis can result in fugitive losses and can present problems to operating personnel. In addition many of the water-related problems noted for physical coal cleaning may also be applicable.

The primary solid discharge stream associated with many of these processes is gypsum; however, the tendency of the heavy metals to remain with the solid stream may present leaching problems.

4.2.2.2 Synthetic Fuels--

Synthetic fuel processes involve conversion of coal to a liquid or gas and the production of oil from oil shale. Substitution of these synthetic fuels for coal can reduce SO_x emissions because chemical reactions remove sulfur during the conversion processes. Technology for production of synthetic fuels is being developed to incorporate pollutant control technology.

Coal conversion--Synthetic gas or oil is produced by allowing coal to react with hydrogen and oxygen in the presence of catalysts or solvents while applying heat and pressure. In most of the processes sulfur is released from the coal as hydrogen sulfide, which can then be scrubbed from the gases and converted to elemental sulfur. Further technological development and more favorable economics are needed before any of the myriad of conversion processes can reduce SO_x emissions significantly.[28]

Coal gasification processes are often categorized as low-, medium-, or high-Btu systems, in accordance with the heating value of the product. Each system includes coal pretreatment, gasification, and gas cleaning steps. Low- and medium-Btu gas was produced from coal for many years before cheap natural gas became available. If and when production again becomes economical, such gas will probably be used first in process heaters and steam boilers.[29]

Gasification in conjunction with combined-cycle power plants will probably prove economically feasible for the utility industry, but technical improvements in gas turbines and in the efficiency of coal gasifiers are needed.[30],[31] High-Btu synthetic gas will probably be too expensive for widespread use in large combustion units but could eventually supplement diminishing natural gas supplies for use in residential heating.[32]

Nearly 70 different coal gasification processes are under development or have been operated commercially. Table 4.2-9 lists the coal gasification processes that are considered most promising.[33]

TABLE 4.2-9. COAL GASIFICATION SYSTEMS[33]

Commercially available	Commercially demonstrated or under construction
Chapman[a]	
Foster-Wheeler/Stoic	BGC/Lurgi Slagging Gasifier
Koppers-Totzek	Bi-Gas
Lurgi	Coalex
Wellman Incandescent	Pressurized Wellman-Galusha
Wellman-Galusha	Riley Morgan
Winkler	Texaco
Woodall Duckham/Gas Integrale	

[a] Since publication of Reference 33, the Chapman gasifier has become commercially available.

As with coal gasification, the technology for coal liquefaction has been available for some time. During World War II, Germany produced transport fuel and 90 percent of its aviation fuel from coal.[34] Research and further development of coal liquefaction in the United States was minimal until it was realized that domestic oil supply is not infinite and that oil may not always be available from foreign suppliers.[35]

Coal liquefaction is similar to gasification. The ratio of hydrogen to carbon is increased in the progression from coal to synthetic oil to synthetic gas.[36,37] Coal liquefaction processes generate an acid gas stream containing sulfur and other contaminants. As with coal gasification processes, removal of hydrogen sulfide and recovery of sulfur may be necessary.[38]

One solvent-refined coal method (SRC-I) is being investigated as a method to convert coal to clean solid boiler fuel and liquid fuel products. As in coal gasification and liquefaction, the SRC-I process increases the hydrogen content of the coal, but to a lesser extent in order to reduce processing costs.[39] In tests, the process has reduced the ash content of coal to 0.1 to 0.2 percent[40] and has removed 71 to 93 percent of the total sulfur content.[41] Reduction of SO_x emissions would therefore appear to be comparable with that achieved through chemical coal cleaning processes. Major advantages of SRC-I are that most utilities are already equipped to fire solid coal, the operation and maintenance of ash handling equipment is reduced, and pulverizer maintenance will probably be reduced because SRC-I is easier to pulverize.[39,42]

Another solvent-refined coal method (SRC-II) produces only liquid products. The resulting low-sulfur liquid fuel is being investigated as a replacement for fuel oil and as a compliance fuel.

Shale oil--The energy potential of shale oil in the United States is second only to that of our vast coal reserves. Although shale oil development has occurred sporadically in the United States since the 1800's, no shale oil is now produced commercially.[43] Recent emphasis on energy self-sufficiency has spurred development of this resource.[44] Several different methods of retorting the shale (applying heat to release the oil) are under investigation.[43] With respect to SO_x emissions, oil from shale appears very attractive because the sulfur content is relatively low, 0.5 to 0.7 percent by weight.[45]

The major problems associated with shale oil recovery are the handling and disposal of the vast quantities of solid waste associated with the oil recovery process and the demand for water, which is required for the process but which may not be available in areas where the shale oil is located.

4.2.3 Flue Gas Desulfurization[46,47]

Flue gas desulfurization (FGD) has become a leading means of controlling SO_x emissions in the United States; it is primarily used by the electric utility industry. The operating capacity of FGD systems has risen sharply from 900 MW in the pilot plant era of the late 1960's to about 25,000 MW in 1979 and is projected to reach about 62,000 MW by 1986.[46] It is estimated that as of late 1979, the total operational FGD capacity on utility boilers was 25,000 MW, roughly equivalent to 2.8 Tg (3 million tons) of annual SO_2 removal.

Dry or wet FGD systems can be used to control SO_x emissions; wet systems, however, dominate the entire utility market in the United States.

Flue gas desulfurization processes are categorized as regenerable or nonregenerable depending on whether sulfur compounds are separated from the absorbent as a byproduct or disposed of as a waste. Nonregenerable processes produce a sludge that requires disposal in an environmentally sound manner. Regenerable processes have additional steps to produce byproducts such as liquid SO_2, sulfuric acid, and elemental sulfur. The nonregenerable group includes processes such as lime and limestone, sodium carbonate, and double alkali FGD systems. The regenerable systems currently in operation are typified by the magnesium oxide and the Wellman-Lord systems.

A listing of all the operable utility FGD systems as of June 1979 is given in Table 4.2-10.[47] This table shows the equivalent MW of the gas treated, the FGD process, and whether the system is a new or a retrofit installation. Utility systems account for the bulk of the boiler flue gas treated in the United States.

During test periods, all the major wet FGD processes in current use (lime, limestone, double alkali, Wellman-Lord, and magnesium oxide) have demonstrated high SO_2 removal capabilities.[48] It is important to note that most test data concerning SO_2 removal efficiency are from a number of individual tests run on various days and do not necessarily reflect long-term performance. Because many problems have arisen regarding the use of continuous SO_2 monitors for inlet and outlet SO_2 concentrations, most data in the literature are for short-term SO_2 removal tests, and sometimes at different operating conditions. Such tests are not representative of long-term averages. Averaging times are not normally reported even for short-term tests. The U.S. EPA Method 6 is the test procedure normally used for determination of SO_2 emissions from stationary sources.

In this FGD section the following terms are used: availability, reliability, operability, and utilization. Definitions of these words are as follows:

Availability Index	Hours the FGD system is available for operation (whether operated or not) divided by hours in period, expressed as a percentage.
Reliability Index	Hours the FGD system was operated divided by the hours the FGD system was called upon to operate, expressed as a percentage.
Operability Index	Hours the FGD system was operated divided by boiler operating hours in period, expressed as a percentage. This parameter indicates the degree to which the FGD system is actually used, relative to boiler operating time.

TABLE 4.2-10. OPERATING FGD SYSTEMS: JUNE 1979[47]

Company/Unit name	No.	MW (ESC)	Process	New/retrofit	Start date
Alabama Electric Coop					
Tombigbee	2	179	Limestone	New	9/78
Tombigbee	3	179	Limestone	New	6/79
Allegheny Power System					
Pleasants	1	519	Lime	New	3/79
Arizona Electric Power Coop					
Apache	2	195	Limestone	New	8/78
Apache	3	195	Limestone	New	6/79
Arizona Public Service					
Cholla	1	119	Limestone	Retrofit	10/73
Cholla	2	350	Limestone	New	4/78
Central Illinois Light					
Duck Creek	1	416	Limestone	New	9/76
Columbus & Southern Ohio Elec.					
Conesville	5	411	Lime	New	1/77
Conesville	6	411	Lime	New	6/78
Duquesne Light					
Elrama	1-4	510	Lime	Retrofit	10/75
Phillips	1-6	410	Lime	Retrofit	7/73

Note: ESC is Equivalent Scrubbed Capacity, which is the effective scrubbed flue gas volume based on the percentage of the flue gas scrubbed by the FGD system.

(continued)

TABLE 4.2-10 (continued)

Company/Unit name	No.	MW (ESC)	Process	New/retrofit	Start date
Gulf Power					
Scholz	1,2	23	Limestone/Thoroughbred	Retrofit	8/78
Indianapolis Power & Light					
Petersburg	3	532	Limestone	New	12/77
Kansas City Power & Light					
Hawthorn	3	90	Lime	Retrofit	11/72
Hawthorn	4	90	Lime	Retrofit	8/72
La Cygne	1	874	Limestone	New	2/73
Kansas Power & Light					
Jeffrey	1	540	Limestone	New	8/78
Lawrence	4	125	Limestone	Retrofit	1/76
Lawrence	5	420	Limestone	Retrofit	11/71
Kentucky Utilities					
Green River	1-3	64	Lime	Retrofit	9/75
Louisville Gas & Electric					
Cane Run	4	188	Lime	Retrofit	8/76
Cane Run	5	190	Lime	Retrofit	12/77
Cane Run	6	288	Dual alkali	Retrofit	4/79
Mill Creek	3	442	Lime	New	8/78
Paddy's Run	6	72	Lime	Retrofit	4/73

(continued)

TABLE 4.2-10 (continued)

Company/Unit name	No.	MW (ESC)	Process	New/retrofit	Start date
Minnkota Power Cooperative					
Milton R. Young	2	405	Lime/Alkaline flyash	New	9/77
Montana Power					
Colstrip	1	360	Lime/Alkaline flyash	New	9/75
Colstrip	2	360	Lime/Alkaline flyash	New	5/76
Nevada Power					
Reid Gardner	1	125	Sodium carbonate	Retrofit	4/74
Reid Gardner	2	125	Sodium carbonate	Retrofit	4/74
Reid Gardner	3	125	Sodium carbonate	New	6/76
Northern Indiana Public Service					
Dean H. Mitchell	11	115	Wellman Lord	Retrofit	7/76
Northern States Power					
Sherburne	1	740	Limestone/Alkaline fly ash	New	3/76
Sherburne	2	740	Limestone/Alkaline fly ash	New	4/77
Pennsylvania Power					
Bruce Mansfield	1	917	Lime	New	12/75
Bruce Mansfield	2	917	Lime	New	7/77
Philadelphia Electric					
Eddystone	1A	120	Magnesium oxide	Retrofit	9/75
Public Service of New Mexico					
San Juan	1	361	Wellman Lord	Retrofit	4/78
San Juan	2	350	Wellman Lord	Retrofit	8/78

(continued)

TABLE 4.2-10 (continued)

Company/Unit name	No.	MW (ESC)	Process	New/retrofit	Start date
South Carolina Public Service					
Winyah	2	140	Limestone	New	7/77
Southern Illinois Power Coop					
Marion	4	184	Limestone	New	5/79
Southern Indiana Gas & Elec					
A.B. Brown	1	265	Dual alkali	New	3/79
Southern Mississippi Electric					
R.D. Morrow	1	124	Limestone	New	8/78
R.D. Morrow	2	124	Limestone	New	6/79
Springfield City Utilities					
Southwest	1	194	Limestone	New	4/77
Tennessee Valley Authority					
Shawnee	10A	10	Lime/Limestone	Retrofit	4/72
Shawnee	10B	10	Lime/Limestone	Retrofit	4/72
Widows Creek	8	550	Limestone	Retrofit	5/77
Texas Utilities					
Martin Lake	1	595	Limestone	New	4/77
Martin Lake	2	595	Limestone	New	5/78
Martin Lake	3	595	Limestone	New	2/79
Monticello	3	800	Limestone	New	5/78
Utah Power & Light					
Hunter	1	360	Lime	New	5/79
Huntington	1	366	Lime	New	5/78

Utilization Index	Hours that the FGD system operated divided by total hours in period.

In addition to the type of FGD system installed, much interest has been focused on the cost of these systems and also the difference between new and retrofit installations. In March 1978, an EPA-sponsored FGD system cost study was conducted on each utility having at least one operable FGD system; these costs were adjusted to a common base time period and were evaluated on a common cost basis. The reported and adjusted costs of the utility FGD systems are shown in Table 4.2-11;[49] the costs shown as the adjusted costs are for a June 1979 base. (The basis used to adjust the costs is available.[50])

The retrofit FGD systems often require higher capital costs than comparable new systems because the systems must be built within space limitations imposed by existing plant facilities. The layout of existing plant facilities governs the location of FGD system equipment. The space availability for scrubbing equipment has a major impact on the cost of the system. The actual space required for the scrubbing equipment is not large; however, the equipment must be located near the existing stack to minimize extensive duct runs. The support facilities such as feed preparation and sludge treatment can be located away from the stack and in a manner required by the existing plant facilities without significant cost increments.

In general, the existing plants are built with compact layouts to minimize the duct runs and without an allowance for additional equipment items such as scrubbing units. In some cases the boiler stacks are located on the roof to take advantage of the elevation. These plants may require long duct runs or construction of a new stack.

For nonregenerable FGD's consideration must be given to land required for disposal of the sludge. The disposal area needed will depend upon factors such as FGD capacity, SO_2 removal rate, and capacity factor; however, these areas could be hundreds of acres over the life span of the FGD system. If onsite disposal of sludge is not possible, then it will have to be pumped or trucked to a disposal site, which will increase the operating costs of the systems.

TABLE 4.2-11. CATEGORICAL RESULTS OF THE REPORTED AND ADJUSTED CAPITAL AND ANNUAL COSTS FOR OPERATIONAL FGD SYSTEMS[49]

Category	Reported[a]						Adjusted					
	Capital, $/kW			Annual, mills/kWh			Capital, $/kW			Annual, mills/kWh		
	Range	Avg	Dev[b]	Range	Avg	Dev[b]	Range	Avg	Dev[b]	Range	Avg	Dev[b]
All	5.3-156.9	77.0	36.9	0.3-14.9	6.3	5.1	70.6-270.2	109.2	40.8	3.1-14.4	6.4	2.8
New	5.3-120.6	71.4	30.0	0.3-14.3	4.6	5.0	76.9-136.3	99.1	19.6	3.2-10.1	6.0	2.3
Retrofit	29.2-156.9	83.7	42.7	2.1-14.9	8.3	4.4	70.6-270.2	120.0	53.1	3.1-14.4	6.7	3.0
Throwaway product	5.3-120.6	67.1	29.2	0.3-14.3	5.9	4.9	70.6-162.9	100.8	24.6	3.1-10.1	6.0	2.2
Saleable product	93.3-156.9	132.5	23.5	3.3-14.9	9.1	5.8	156.2-270.2	213.2	57.0	14.4-14.4	14.4	0.0
Limestone	5.3-99.5	61.4	27.6	1.6-3.3	2.2	0.8	76.9-136.3	107.9	25.4	3.4-7.6	5.8	1.6
Lime	29.2-120.6	74.1	29.7	0.3-14.3	9.0	4.5	78.2-162.9	103.0	24.4	3.2-10.1	7.0	2.3
Lime/Alkaline fly ash	85.9-85.9	85.9	0.0	0.0	0.0	0.0	107.8-107.8	107.8	0.0	6.0-6.0	6.0	0.0
Sodium carbonate	42.9-113.6	66.5	33.3	2.1-2.1	2.1	0.0	70.6-125.0	88.8	25.7	3.7-5.1	4.2	0.7
Wellman Lord	127.9-156.9	137.6	13.7	14.9-14.9	14.9	0.0	156.2-156.2	156.2	0.0	14.4-14.4	14.4	0.0
Limestone/Alkaline fly ash	47.9-47.9	47.9	0.0	2.0-2.0	2.0	0.0	82.9-82.9	82.9	0.0	3.2-3.2	3.2	0.0
Magnesium oxide	156.7-156.7	156.7	0.0	0.0	0.0	0.0	270.2-270.2	270.2	0.0	0.0	0.0	0.0

[a] Actual costs reported in the unadjusted form.

[b] DEV is standard deviation.

The market for recovered sulfur byproducts can determine the economic feasibility of regenerable processes. A byproduct market in the vicinity of the FGD installation reduces the operating costs by the amount received from byproduct sales, whereas nonavailability of a market or location some distance away from the FGD installation may add to the operating cost by the amount required for byproduct disposal.

Nonregenerable FGD processes produce significant amounts of sludge that must be disposed of in an environmentally sound manner. The quantity of sludge that must be handled will vary greatly depending upon the sulfur content of the fuel fired, the absorbent utilized, the FGD system removal efficiency, the degree of oxidation of the sludge, the degree of sludge dewatering achieved, the use of fixation agents, and other variables. In addition, some FGD installations remove fly ash, which combines with the sludge. Disposal areas must be available in the vicinity to minimize transportation costs. An FGD system at a 1000-MW power plant, for example, may generate from 190,000 to 470,000 Mg (210,000 to 515,000 tons) of sludge per year on a dry basis, not including the fly ash, assuming a calcium-based (lime or limestone) FGD system and the firing of coal in the 3.5 to 7.0 percent sulfur range.[51] By 1998, the application of 90 percent SO_2 removal to all new electric generating plants is estimated to result in the production of 157 Tg (173 million tons) (dry basis) of waste per year.[52] The actual quantities of untreated wastes requiring disposal are at least double that amount, assuming a solids content of 50 percent or less.[52]

Coal-fired power plants in the United States have been disposing of coal ash by ponding or landfilling for many years and have extended these conventional ash disposal practices to the disposal of FGD sludge. Several utilities, however, chemically treat or fix the wastes before disposal. Fixation improves the structural properties of the waste and tends to decrease leaching.

At present, no Federal criteria specifically apply to FGD sludge disposal, but the Resource Conservation and Recovery Act of 1976, which was signed into law in October 1976, requires that the EPA establish regulations or guidelines for disposal of wastes from air pollution control systems such as FGD.[53] Guidelines for FGD sludge and coal ash disposal have been prepared and are under review. The EPA has been directing efforts since mid-1975 toward preparation of documents that can be used to set FGD waste disposal guidelines.[54]

The EPA has indicated that disposal of raw sludge is unacceptable. In September 1975, the EPA declared "permanent land disposal of raw (unfixated) sludge to be environmentally unsound because it indefinitely degrades large quantities of land."[55] Eventually, however, disposal of raw FGD sludge may be allowed if means of containing it are proved to be environmentally acceptable. Chemical fixation or seepage elimination through the use of impermeable liners are both possible methods by which FGD wastewaters can meet current criteria for groundwater or drinking water quality.

Approximately 10 state regulatory agencies have considered FGD sludge disposal. They have allowed ponding of untreated sludges, landfilling of fixed sludges, and discharge of excess water.[55]

Currently it appears that ponding with a liner or in an impermeable basin will probably be satisfactory as long as land reclamation is not necessary. Analyses show that FGD sludge can contain toxic trace elements;[56],[57] therefore sludge leachate or overflow and runoff are possible sources of ground water and surface water contamination.[57] If sound structural properties are required, chemical fixation of the sludge, possibly in conjunction with an impermeable basin, would provide sufficient strength and minimize leaching to ground water. Chemical fixation also reduces disposal volume.

Ocean dumping and mine disposal are also possible alternatives for sludge disposal which have been actively investigated by the EPA.[58] Mine disposal also has a potential side benefit of preventing mine subsidence.

The subject of sludge handling and treatment is addressed in a number of other recent reports, in addition to those referenced previously here.[59-66]

The physical and chemical properties of FGD sludge affect the choice of alternatives for handling and disposal and also any possible future land use. Primary sludge constituents that affect the chemical and physical properties are water, fly ash, calcium sulfate, and/or sulfite. Spent slurry drained from an FGD system can contain as much as 85 to 95 percent water.[67] The spent slurry is partially dewatered and thickened to a heavy wet sludge before its ultimate disposal.

Generally, the sludge components of calcium-based FGD sludge consist of calcium sulfite hemihydrate, calcium sulfate dihydrate, fly ash, and unreacted absorbent. The relative amounts of each depend on many factors, including the kind and amount of fuel burned, the efficiency of sulfur dioxide and particulate removal, the purity of the absorbent, and the boiler type and operating practices. Sulfate sludges are more easily dewatered than sulfite sludges and thus result in smaller volumes to be handled. Generally, the higher the water content in the sludge, the less desirable are its physical characteristics. Sulfate sludges are less thixotropic than sulfite sludges. Thixotropic materials will flow or deform upon agitation, which affects structural properties and subsequent land utilization.[68] On the other hand, sulfates are more soluble and have high permeability, which may create landfilling problems for sulfates. In some instances, to meet regulatory requirements, a river may be required. If a leachate removal system is installed, discharging of large quantities of generated leachate will be required.

Direct landfilling of FGD sludge is possible by dewatering the sludge to a high-solids cake. Although high-solids filter cake has been obtained, very little data have been developed on filtration requirements. The energy and filtering capacity requirements for producing a high-solids sludge in a cake form may prove this alternative to be economically unattractive.

The permeability of FGD sludge is a measurement of the rate at which water can pass through the material. Untreated scrubber sludge has a permeability of 10^{-4} to 10^{-5} cm/s, which is approximately the same as fine sand.[69] As a comparison fixed sludge is reported to have a permeability of 10^{-5} to 10^{-7} cm/s.[70]

Elements can be leached from the sludge solids and carried into the underlying soil as liquids move through the sludge. Leachate composition is a function of the chemical composition of the sludge, the solubility of the elements present, pH, and the age of the disposal site. It is important to determine the rate of pollutant migration and the chemical composition of the seepage. The U.S. Army Corps of Engineers and others have been conducting such research for the EPA for several years.[71]

The quantities and physical characteristics of sludge warrant serious consideration of land use and reclamation problems. If the sludge is not treated, it may not remain sufficiently dry to support loads. Over a 20-yr period, a 1000-MW power plant could require an area 3.5 to 4.5 km^2, 3 m deep (860 to 1100 acres, 10 ft deep) to dispose of lime FGD sludge on a dry basis.[54]

Reclamation of disposal sites depends on the load-bearing capacity of the waste. The thixotropic nature of a sulfite sludge could prevent reclamation and pose a permanent hazard. Sludge that has been sufficiently dewatered and is nonthixotropic could be reclaimed and revegetated to produce an area adequate for recreation or building.[54]

Although FGD sludge could be used to produce gypsum for use in wallboard or Portland cement, most utility power plants will dispose of the sludge. Sludge utilization may not be economically attractive at the present time.[72]

4.2.3.1 Lime Process--

The lime process is a wet, nonregenerable SO_2 absorption process, in which an alkaline slurry formed from the lime is circulated through a scrubber/absorber tower, where it reacts with SO_2 in the flue gas. Calcium sulfite and sulfate formed by the reaction are then separated in settlers or clarifiers and filters. The sludge produced by the system can be chemically stabilized to produce an inert landfill material or can be stored in sludge ponds equipped with adequate barriers to prevent contamination of surface or ground waters.

Lime FGD systems have demonstrated the ability to remove in excess of 90 percent of the inlet SO_2 at a number of utility boiler installations in individual, site-specific tests.[73],[74] Facilities at which high removal efficiencies have been obtained are briefly described as follows:[75]

1) The Mohave Station of the Southern California Edison Company reported SO_2 removal efficiency of 98 percent with lime. The tests were conducted intermittently over 1 year on low-sulfur coal. The unit was a 170-MW equivalent, prototype scrubber. The operation of the unit has been terminated.

2) Recent short-term tests at the Paddy's Run Station of Louisville Gas and Electric have shown SO_2 removal efficiencies in excess of

99 percent on 3 percent sulfur coal. This extremely high removal efficiency is attributed to the addition of magnesium oxide to the lime slurry.

3) Several tests were conducted at the 10-MW TVA Shawnee Pilot Plant, where SO_2 removal efficiencies of 95 to 99 percent were reported for lime-based systems.

4) At Bruce Mansfield Station of Pennsylvania Power, SO_2 removal efficiency of 93.2 percent was reported for an FGD on Unit 1 for a short-term period in September 1977.[76]

Process chemistry--The following reactions take place in the absorber during SO_2 absorption by an aqueous scrubbing liquor:

(1) $SO_2(g) \rightarrow SO_2(aq)$

(2) $SO_2(aq) + H_2O \rightarrow H_2SO_3 \rightarrow HSO_3^- + H^+$

(3) $HSO_3^- \rightarrow H^+ + SO_3^=$

Lime in the slurry produces calcium through the following reactions:

(4) $CaO + H_2O \rightarrow Ca(OH)_2(s)$

(5) $Ca(OH)_2(s) \rightarrow Ca(OH)_2\ (aq)$

(6) $Ca(OH)_2(aq) \rightarrow Ca^{++} + 2OH^-$

Sulfite ion generated (Reaction 3) combines with calcium generated (Reaction 6) to yield the insoluble calcium sulfite hemihydrate:

(7) $Ca^{++} + SO_3^= + 1/2H_2O \rightarrow CaSO_3 \cdot 1/2H_2O$

In addition, sulfite ion may ultimately be converted to gypsum in the following reactions:

(8) $SO_3^= + 1/2O_2 \rightarrow SO_4^=$

(9) $Ca^{++} + SO_4^= + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O(s)$

Quantities of lime required by the process and sludge generated in the process are calculated from Reactions 1 through 8. With assumptions of 95 percent lime purity and a 1.0 molar stoichiometric ratio, the lime requirement is 1.05 weight per unit weight of SO_2 removed.

The sludge produced in the process consists of calcium sulfite hemihydrate and gypsum, lime impurities, and any excess lime. The exact proportions of calcium sulfite hemihydrate and gypsum are primarily functions of the SO_2 content of the flue gas, the percent excess oxygen, and whether forced oxidation is applied. An assumption of equal proportions gives a sludge formation rate of 2.5 weight units per weight unit of SO_2 removed. Because the FGD sludge is always generated wet, the weight of associated water must be included.

System description--The equipment for a lime FGD system is generally grouped under four major operations:

- Scrubbing or absorption--includes SO_2 scrubbers, holding tanks, and circulation pumps
- Flue gas handling--includes inlet and outlet ductwork, dampers, reheaters, and fan
- Lime handling and slurry preparation--includes lime unloading and storage equipment, and lime processing and slurry preparation equipment
- Sludge processing--includes clarifier and filters (if used) for sludge dewatering, sludge pumps, and sludge handling equipment

A diagram of a typical lime FGD system is shown in Figure 4.2-4. Individual systems may deviate from that shown, depending upon plant characteristics and system manufacturer.

A forced draft fan (not shown in the figure) forces the flue gas via ducting and dampers through the absorber, in which the SO_2 is transferred from the flue gas to the circulating slurry. The flue gas then passes through a mist eliminator to a heat exchanger, where the flue gas is often heated to about 80°C (175°F) before it is exhausted to the atmosphere. Reheating the flue gas reduces the possibility that condensation of water vapor, with its attendant acidification as sulfur oxides are absorbed, will create a corrosive environment for the ducting, stack, and the fan, if an induced draft fan were used. Reheat also increases the plume buoyancy. A number of reheat plans are in use or have been suggested to reduce the heat/energy requirement.[77]

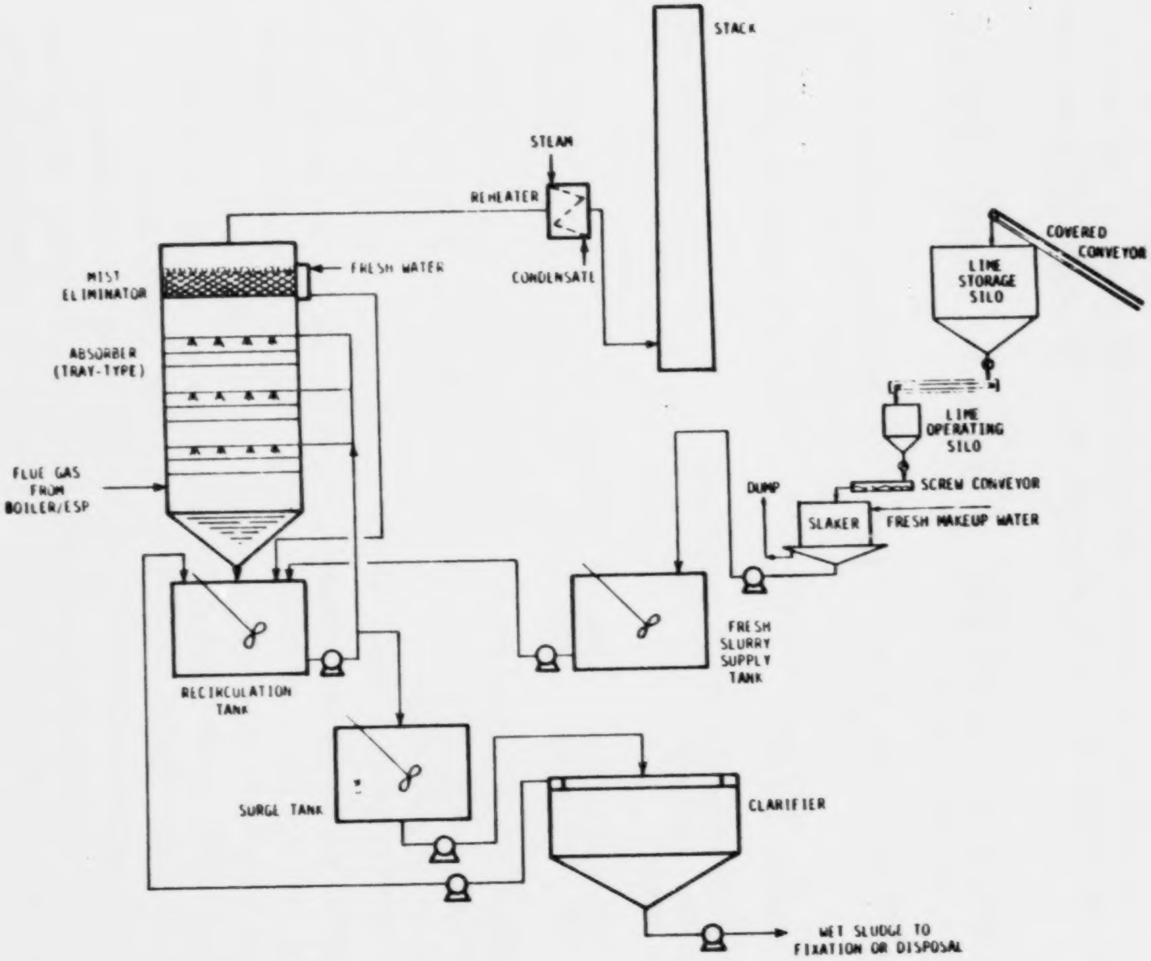
STACK
STEAM
REHEATER
CONDENSATE
COVERED CONVEYOR
LIME STORAGE SILO
MIST ELIMINATOR
FRESH WATER
ABSORBER (TRAY-TYPE)
LIME OPERATING SILO
FLUE GAS FROM BOILER/ESP
DUMP
SCREW CONVEYOR
SLAKER
FRESH MAKEUP WATER
FRESH SLURRY SUPPLY TANK
RECIRCULATION TANK
SURGE TANK
CLARIFIER
WET SLUDGE TO FIXATION OR DISPOSAL

Figure 4.2-4. Typical lime FGD system.

Slurry from the absorber goes to the hold tank, from which a fixed amount of slurry is bled off and sent to the sludge circuit; an equal amount of fresh lime slurry is added to the hold tank. Lime handling and slurry preparation require lime unloading equipment, lime storage silos, conveyors, a lime slaker, grit removal equipment, and slurry tanks.

The sludge must be dewatered to make it suitable for disposal. Water recovered from the sludge dewatering circuit is returned to the scrubbing circuit to maintain a closed loop system to prevent direct contamination of fresh water supplies with effluent and to confine products of FGD to the sludge. In most FGD installations in the United States, the sludge solids are allowed to settle in a holding pond on the site. Flow to the holding pond either comes directly from the recirculation tank or from the clarifier (as partially dewatered sludge). Water from the sludge pond is returned to the scrubbing circuit.

The availability of an FGD system is in most part dependent upon the availability of the absorbers, whose basic function is to promote contact between SO_2-laden gas and calcium in the circulating slurry. A residence time of 1 to 4 seconds is necessary for effective SO_2-calcium contact. The two major parameters of an absorber-liquid to gas ratio (L/G) and the typical pressure drop are functions of the absorber configuration and type, the SO_2 removal required, and the inlet SO_2 content of the gas stream. The energy requirement of an absorber is made up of two components: 1) the energy needed to overcome the system pressure drop and 2) that needed to circulate the lime slurry. To achieve maximum SO_2 removal with an optimum amount of energy input, industry operators use various types of absorbers. The major types are discussed in the following paragraphs.

Tray absorber[78]--A tray absorber promotes gas-slurry contact in a vertical column with transversely mounted perforated trays. The SO_2-laden gas enters at the bottom of the column and travels upward through the perforations in the trays; the reagent slurry is fed at the top and flows toward the bottom. Absorption of SO_2 is accomplished by countercurrent contact between the gas and reagent slurry.

A schematic drawing of a tray scrubber is shown in Figure 4.2-5.

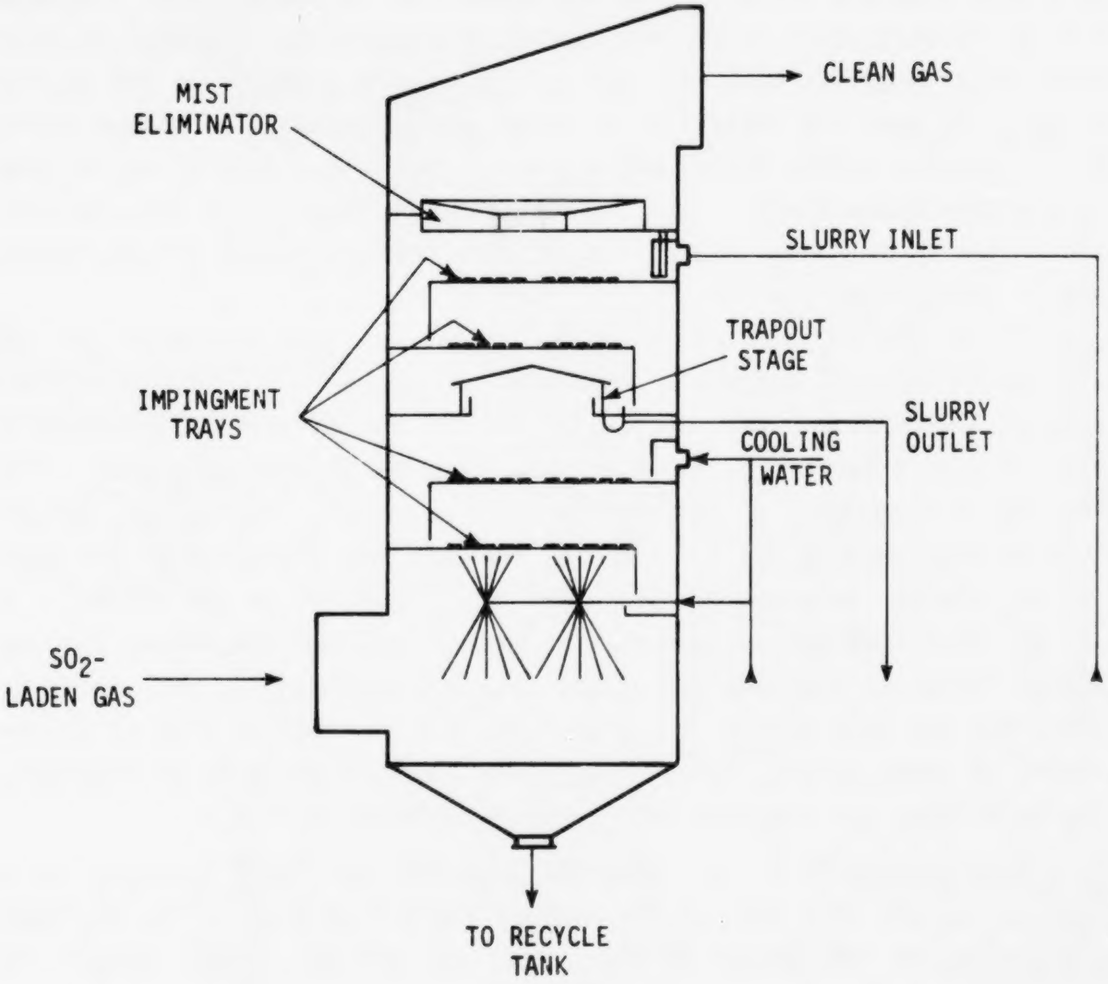
MIST ELIMINATOR
CLEAN GAS
SLURRY INLET
TRAPOUT STAGE
IMPINGMENT TRAYS
SLURRY OUTLET
COOLING WATER
SO$_2$- LADEN GAS
TO RECYCLE TANK

Figure 4.2-5. Tray absorber.

Packed scrubber[79]--A packed scrubber consists of an absorption tower filled with packing material designed to provide a large surface area for gas/liquid contact. The reagent slurry is fed at the top and travels downward, wetting the packing surfaces; the gas travels upward from the bottom through the packing material. The packed tower design offers a large area for contact of reagent and SO_2-laden gas and provides the longest residence time among all of the scrubber types.

These absorbers require careful control of reagent flow rates, which must be high enough to prevent blowing and dry gas channeling, but not so high as to cause flooding. Normal operation is 0.2 to 0.8 kPa/m (0.25 to 1.0 in. H_2O/ft) of packing, corresponding to 40 to 70 percent of the flooding velocity.

Mobile bed scrubber[80]--The mobile bed scrubber, shown in Figure 4.2-6, extends the concept of a tray type scrubber. It consists of perforated trays or grids filled with mobile elements such as plastic spheres and mounted transversely in a vertical column. Flue gas introduced at the bottom travels upward through the mobile packings; the reagent slurry, fed at the top, flows downward. This countercurrent operation, coupled with the action of the mobile spheres on the transverse trays, produces highly turbulent zones in the scrubber. Each sphere is free to rotate, and the constant movement results in self-cleaning of the spheres.

A typical overall pressure drop for a mobile bed scrubber is 1.5 to 2 kPa (6 to 8 in. of H_2O).

Venturi scrubber--In a venturi scrubber the SO_2-laden gas is introduced at the top, passes through a converging section of the scrubber (the venturi throat), and then exits the scrubber through a diverging section. The venturi shape imparts high velocity to the passing gases at the throat. The reagent slurry is also introduced at the throat, leading to turbulent mixing of the gases and reagent slurry. This thorough mixing promotes a chemical reaction between the SO_2 in the gas and the absorbent.

The annular orifice design, as shown in Figure 4.2-7, has the converging section, throat, and diverging section. The gas impinges on either a fixed or movable disc while liquid flows cocurrently down the walls of the

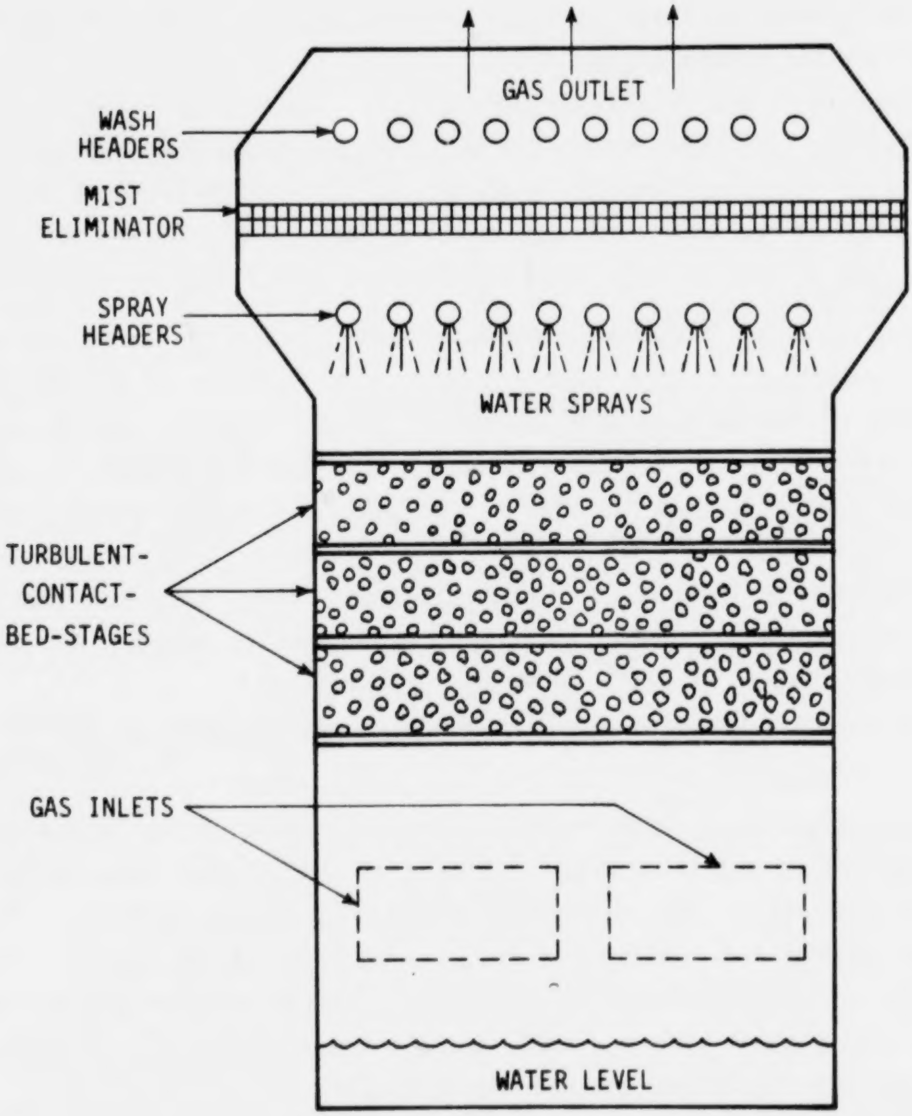
GAS OUTLET
WASH HEADERS
MIST ELIMINATOR
SPRAY HEADERS
WATER SPRAYS
TURBULENT-CONTACT-BED-STAGES
GAS INLETS
WATER LEVEL

Figure 4.2-6. Typical mobile bed scrubber.

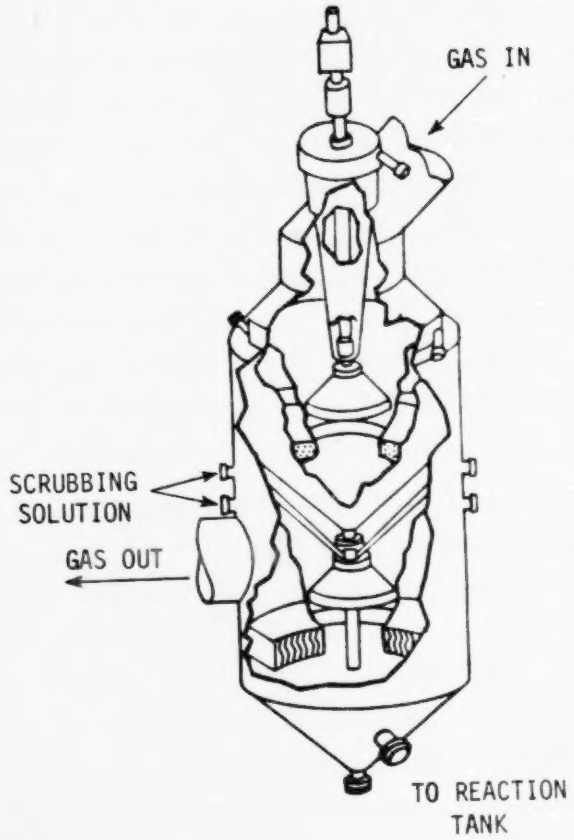
GAS IN
SCRUBBING SOLUTION
GAS OUT
TO REACTION TANK

Figure 4.2-7. Two stage venturi scrubber.

converging section. As the gas stream exits the throat, the gas stream diverges, which accomplishes much of the liquid separation.

In the rod bank tower design, parallel rows of horizontal rods are placed in the throat of the venturi, perpendicular to the gas flow. The reagent slurry is introduced just ahead of the rods and also on the walls of the venturi section.

Spray tower--A spray tower scrubber can be vertical or horizontal. The reagent slurry is introduced in the scrubber in atomized droplets through the spray nozzles at the top. The flow of gas and slurry is crosscurrent in a horizontal design and countercurrent in a vertical design.

Figure 4.2-8 shows a modification of a conventional spray tower scrubber supplied by M.W. Kellogg Company. Slurries of varying degrees of richness can be introduced at the different stages in the tower. Often the fresh slurry (recycle and makeup streams) is introduced at the rear of the absorber (the last stage) where the SO_2 content of the gas stream is lowest. The slurry collected in the last stage is pumped forward to the next stage. In effect, the slurry "flows" countercurrent to the gas flow. The first stage of the absorber has the highest SO_2 concentration gas stream and a slurry that has had much of its active alkalinity exhausted.

Sludge disposal[81-84]--Processing of the sludge generated by an FGD system may involve several steps. A stream is bled continuously from the scrubber to the sludge circuit. Because this stream contains a large proportion of water (90 percent is not uncommon), liquid-solid separation is required. The FGD sludge is thixotropic.

The major constituents of lime FGD sludge and the typical percentages are 73 percent $CaSO_3 \cdot 1/2H_2O$, 11 percent $Ca(OH)_2$, 11 percent $CaSO_4 \cdot 2H_2O$, and 5 percent $CaCO_3$. The percentages vary from system to system.

A typical sludge processing circuit (Figure 4.2-9) involves solids sedimentation, dewatering, fixation, and transportation of sludge for final disposal. Clarifiers are generally used for sedimentation; the recovered water is sent back to the scrubber circuit, and the partially dewatered sludge is sent for further dewatering. When vacuum filters are used for further dewatering, the dewatered cake contains about 60 percent solids. Any further dewatering leads to excessive energy consumption.

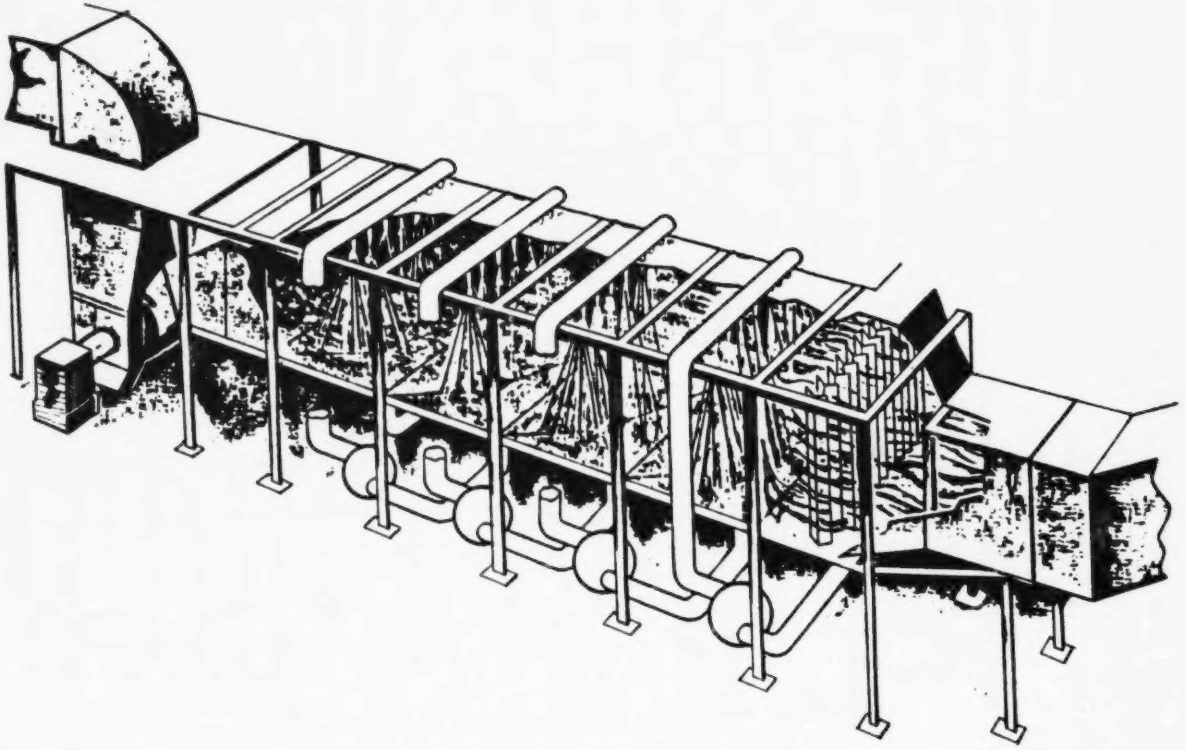

Figure 4.2-8. Horizontal spray scrubber.

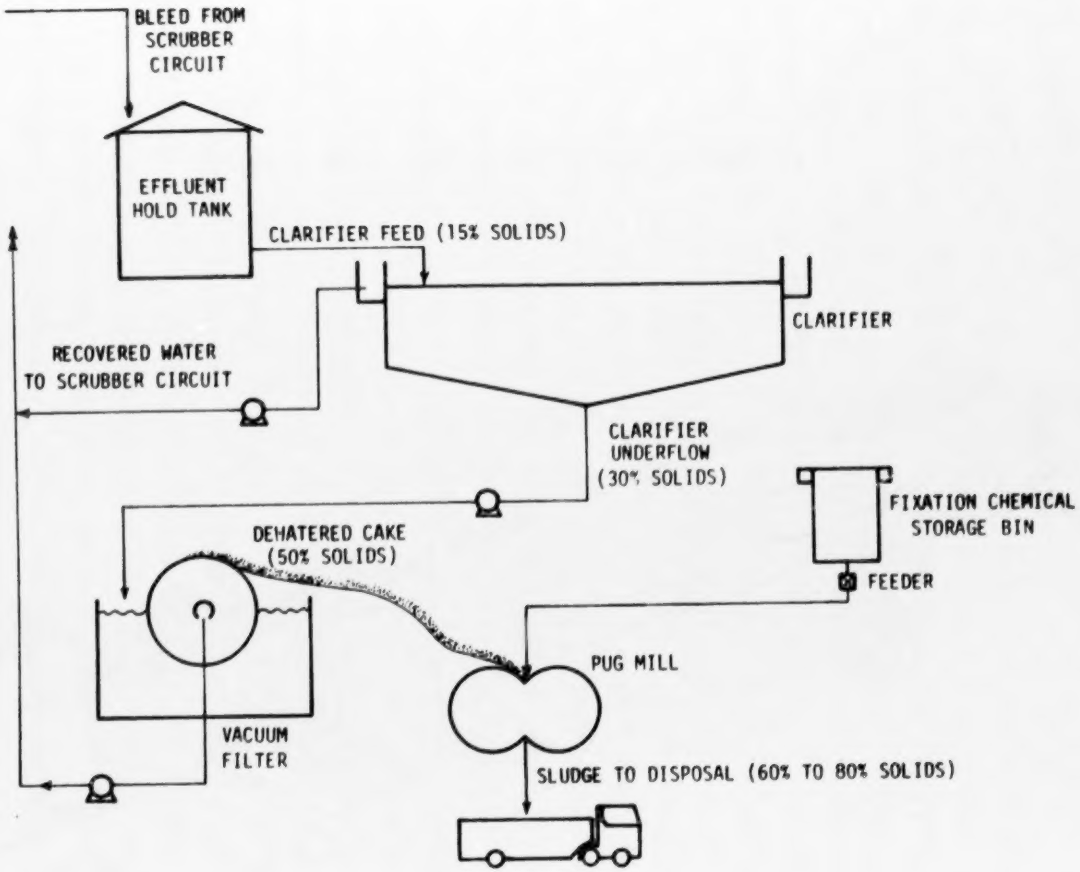
BLEED FROM SCRUBBER CIRCUIT
EFFLUENT HOLD TANK
CLARIFIER FEED (15% SOLIDS)
CLARIFIER
RECOVERED WATER TO SCRUBBER CIRCUIT
CLARIFIER UNDERFLOW (30% SOLIDS)
FIXATION CHEMICAL STORAGE BIN
DEWATERED CAKE (50% SOLIDS)
FEEDER
PUG MILL
VACUUM FILTER
SLUDGE TO DISPOSAL (60% TO 80% SOLIDS)

Figure 4.2-9. Typical sludge processing circuit.

After the vacuum filtration, the cake is transferred to a fixation tank, where chemicals are added to the cake and mixed thoroughly. The fixation process is a means of physically and chemically stabilizing the sludge to reduce its pollution potential and facilitate handling. Two companies, Dravo Corporation and IU Conversion Systems, Inc. (IUCS), have systems in operation at utility FGD sites. The processes of both companies use proprietary fixation agents to produce pozzolanic reactions.

In the Dravo process, a proprietary additive called Calcilox^R is added to the sludge. Calcilox^R is a hardening agent derived from blast furnace slag. The fixed sludge is physically more stable, stronger, and less permeable than untreated sludge.

The IUCS process utilizes pozzolanic (cementitious) reaction principles. The company markets a physico-chemical fixation system called Poz-O-Tec^R, which it claims produces a sludge that is ecologically acceptable. The Poz-O-Tec^R process incorporates the sludge into a chemically stabilized matrix. The sludge is trapped and encapsulated within the hard and relatively impermeable matrix. The process involves addition of lime, dry fly ash, and other substances to the dewatered sludge.

Additional information on sludge handling treatment and disposal can be found in the FGD Sludge Disposal Manual published by Electric Power Research Institute (EPRI FP-977).

Energy and environmental impacts[85-87]--Operation of FGD equipment requires significant amounts of energy. The FGD components consuming major amounts of energy are the ID fan that overcomes pressure drop in the absorber and ductwork, and the process pumps that maintain the flow of fluids in the system. The pressure drop through the absorber depends on such factors as the number of trays, type of packing, the height of the unit, and L/G ratio. Energy is also used in reheating the gases as they leave the absorber before they are discharged to the atmosphere.

Transportation of scrubber sludge to a distant disposal site also consumes energy. This energy may be tapped from the electrical energy generated by the plant if the sludge is transported by pumps.

The energy requirement of the FGD system reduces the capacity of a utility plant by the amount needed to operate the FGD system. For a new plant and FGD installation, the FGD energy requirement can be factored into the design of the generation system, but this will lead to higher initial costs and higher annual amortization charges. At existing plants where an FGD system is retrofitted, the energy must be tapped from that generated by the plant for sale. Some installations may be required to compensate for the reduced capacity by purchasing the additional energy from a power pool at higher cost.

The loads for utility boilers vary during the day according to electricity demand. When a boiler is not operating at or near its rated capacity, the energy requirement of an FGD can be met by generating additional energy. When a boiler is operating at or near its rated capacity, the additional energy requirement must be purchased from a power pool or other sources.

The concept of capacity penalty is illustrated in Figure 4.2-10, in which a hypothetical load demand curve is assumed. The solid horizontal line shows the maximum rated generating capacity of the plant. The solid curve indicates the load demand curve; the dotted curve indicates the total plant load with its FGD operating. For the illustrated plant, the total energy demand exceeds the generating capacity in the regions indicated as A and B. The shaded areas indicate the amount of energy purchased from outside sources.

The energy requirement of a lime FGD system ranges from 3 to 5 percent of the boiler capacity when 100 percent of the flue gas is treated and reheated. This range excludes the energy required for sludge transportation. The energy required to overcome pressure drop is a function of scrubber type and system configuration. The energy required for reheating flue gases is a function of the degree of reheat and bypass, which in turn depends upon the permissible exit gas temperatures in the stack and ductwork. When only part of the flue gas is treated, the remainder is bypassed directly to the stack. This gas stream is not subjected to temperature drop of the FGD system and is hotter than the gas stream leaving the FGD system; the higher temperature of the bypass stream reduces the amount of reheat needed.

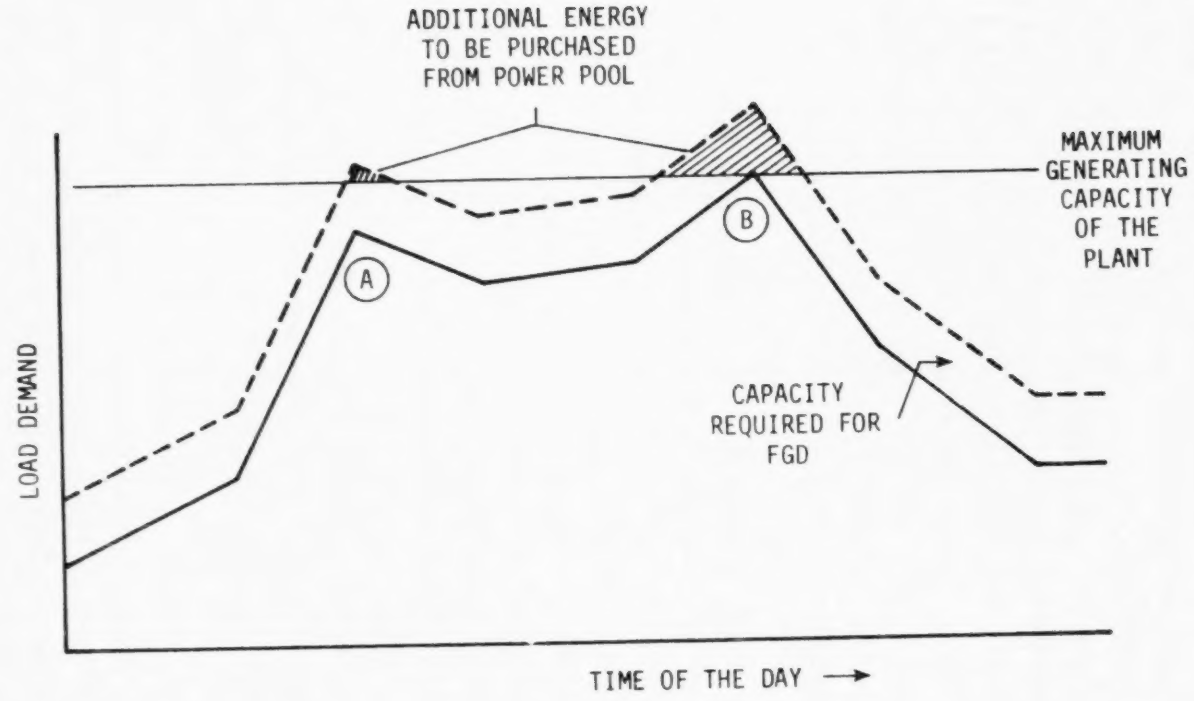
ADDITIONAL ENERGY TO BE PURCHASED FROM POWER POOL
MAXIMUM GENERATING CAPACITY OF THE PLANT
A
B
CAPACITY REQUIRED FOR FGD
LOAD DEMAND
TIME OF THE DAY →

Figure 4.2-10. Illustration of capacity penalty concept.

The amount of bypass will depend upon the SO_2 removal requirements. In general, to meet NSPS no bypass will be possible while firing high-sulfur coal because of high SO_2 removal requirements. When low-sulfur or medium-sulfur coal is fired, however, it may be possible to meet the NSPS by bypassing a fixed quantity of flue gas. The amount of bypass will depend on the applicable NSPS, the sulfur content of the fired coal, and the maximum SO_2 removal potential of the FGD system.

The operation of an FGD imposes energy and capacity penalties on the plant. Figures 4.2-11 and 4.2-12 show the relationships of FGD energy and capacity penalties for a 500-MW plant firing bituminous coal. An energy penalty is represented as the percentage of total generating capacity. The energy used by the FGD system does not depend on averaging time. A capacity penalty represents an instantaneous derating in boiler capacity by the amount required to operate the FGD system. The derating depends upon the maximum power to be reserved for the system during sulfur peaks. This study treats the capacity penalty as a percentage of total generating capacity. Additional information on the energy and environmental impacts of FGD are given in Section 3 of this report. The energy penalty curve is based on a reheat requirement of 28°C (50°F). The sudden change in the slope of the energy penalty curve at a gas flow rate of about 70 percent is due to the need for reheat energy beyond this point. At gas flow rates below this point, the bypass stream temperature provides the needed heat and eliminates the reheat energy requirements.

The environmental impacts of lime FGD are positive with respect to reduction of gaseous pollutant emissions and negative with respect to disposal of sludge. The SO_2 emissions from the system depend on the sulfur content of the boiler fuel. Sulfur dioxide emission rates as low as 50 ng/J (0.12 $lb/10^6$ Btu) could be achieved with a low-sulfur fuel. The emission rates could be as high as 800 ng/J (1.9 $lb/10^6$ Btu) with high-sulfur fuels.

A lime FGD system designed for SO_2 removal can also remove some particulate matter from the incoming gas. In general, a system designed for both particulate and SO_2 removal will require a scrubbing circuit for particulate removal in addition to the SO_2 removal equipment.

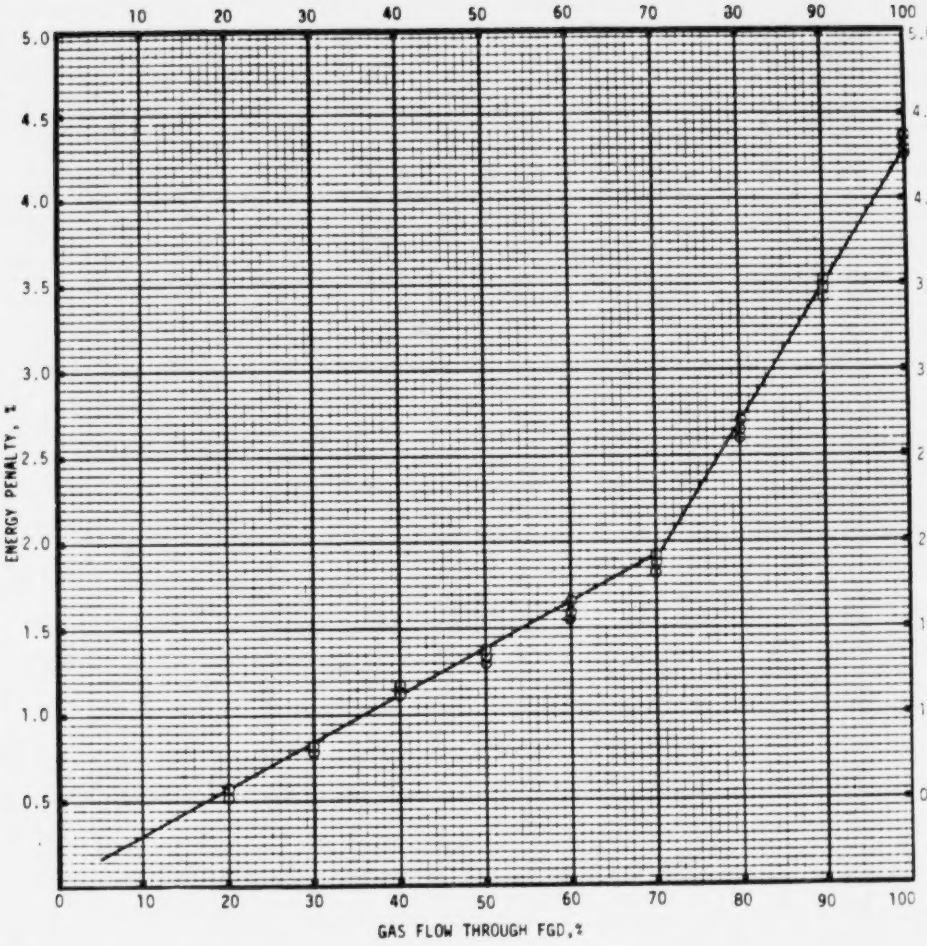

Figure 4.2-11. Energy penalty for a lime FGD system utilizing bypass heat at a bituminous-coal-fired 500-MW plant.[88]

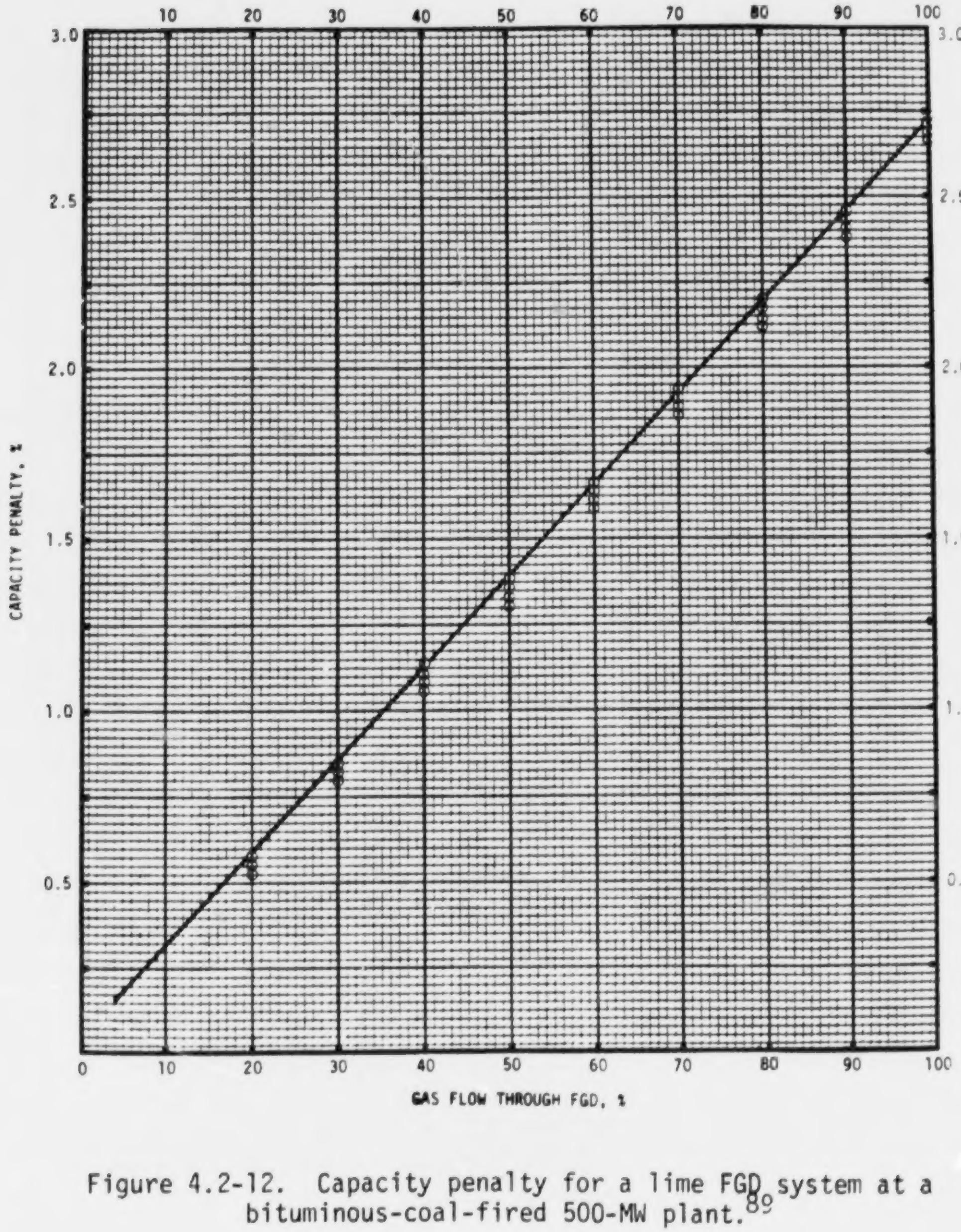

Figure 4.2-12. Capacity penalty for a lime FGD system at a bituminous-coal-fired 500-MW plant.[89]

If the stack gases are not reheated, localized emissions of acid mist may occur. Some of the SO_2 and SO_3 remaining in the flue gas could condense to form sulfurous and sulfuric acid in the stack under such conditions. Proper choice of stack liners can reduce corrosion problems from this condensate.

Sludge disposal is the major potential environmental problem associated with FGD systems. A lime FGD system generates approximately 3 to 5 weight units of sludge (depending on the solids content of the sludge) for each weight unit of SO_2 it removes. A 1000-MW plant burning 3.5 percent sulfur coal and 14 percent ash, would generate about 190,000 Mg (210,000 tons) of FGD sludge per year at 90 percent SO_2 removal efficiency.[90] This plant would consume 2,152,000 Mg (2,373,000 tons) of coal per year and generate 201,000 Mg (222,000 tons) of ash requiring disposal.[90]

Operational status and current developments[91-93]--As of the third quarter of 1979, lime FGD systems represented 24 percent of the total committed capacity for utility FGD systems in the United States. The system is available from various vendors, who are joining with other groups and agencies in major efforts to improve such aspects of the process as chemical control, sludge stabilization, and SO_2 removal efficiency.

The products of reaction have caused plugging and scaling of the absorber in lime FGD systems. Scaling and plugging in lime systems, however, have been relatively insignificant as compared with other calcium-based FGD systems. Scrubber internals and mist eliminator surfaces are most susceptible to scaling; plugging can occur in such components as nozzles and tray passages.

The solutions have been improved for chemical control of the absorbent loop; for example, seed crystals and scrubbers/absorbers with reduced surface area have been used to control precipitation.

In efforts to improve SO_2 removal efficiency, some operators are using reagent additives such as magnesium oxide (MgO) and adipic acid. Dravo Corporation has patented an MgO-promoted lime reagent called Thiosorbic^R lime and claims SO_2 removal efficiencies of 90 percent and greater by U.S. EPA Method 6 tests.

The EPA studied the effects of adipic acid at a pilot plant in North Carolina and at the TVA/EPA Shawnee test facility near Paducah, Kentucky. Adipic acid in concentrations of 700 to 1500 ppm in the scrubber liquor have been reported to yield SO_2 removal efficiencies above 90 percent by U.S. EPA Method 6 tests. The investigators report only minor differences in the processing of sludge and no scaling problems.

System costs[94-96]--Because of differences in system designs and in cost estimating procedures, the costs reported by various FGD installations in the early 1970's varied widely and followed no definite pattern. Most of these systems were the first of a kind and incorporated various safety factors. These early efforts, however, have led to standardization of system design, and the range of reported costs has narrowed. The early efforts have also generated enough data for development of cost models to predict the costs of an FGD system of a given size.

The cost of an FGD system is often presented as a capital cost and an annual cost. Capital costs indicate the total initial investment necessary to install the system. The annualized cost indicates the cost of operating and maintaining the system and also the annual expense of repaying the initial investment; the annualized cost thus represents the total annual revenue requirements of the FGD system.

Capital costs consist of direct and indirect costs incurred up to the successful commissioning date of the facility. Direct costs include the costs of equipment and the labor and material required for installing it and interconnecting the system. Indirect costs are expenditures for the overall facility that cannot be attributed to specific equipment; they include such items as freight and spares.

The annualized costs consist of a capital cost component and an operating cost component. The capital cost component includes the charges for using the capital investment: equipment depreciation, taxes, insurance, and interest paid for capital investment. The operating cost component includes the costs of raw materials, utilities, labor, maintenance and repair, and overhead.

A sensitivity study of the individual cost items of a typical 500-MW FGD system indicates that the SO_2 scrubbing module of the system constitutes a major portion of the capital costs. Table 4.2-12[97] shows the results of such a study. The original costs were estimated on the basis of 3.48 percent sulfur in the coal and 90 percent SO_2 removal. A similar analysis of annualized costs is shown in Table 4.2-13.[97]

Various publications predict the costs of FGD systems. Figures 4.2-13 through 4.2-16 present charts for predicting the value of various components of a lime FGD[98-101] system. The figures are intended for use with a combination of input parameters, the SO_2 removal requirements being a major one. The costs for an FGD can be found by selecting the combination of SO_2 removal requirements and percent of flue gas treated. When the SO_2 removal efficiency required to meet the regulations is lower than the maximum achievable efficiency of the FGD system, partial scrubbing of flue gas is possible. The percent of flue gas requiring SO_2 removal will depend upon the sulfur content of coal, applicable regulations, and maximum possible efficiency of the selected FGD system. The cost basis of these charts is mid-1978 dollars. Figure 4.2-13 shows the capital investment for system equipment excluding the sludge pond and land costs, which are shown separately in Figure 4.2-14. Figure 4.2-15 shows the operation and maintenance cost excluding energy costs. The fixed charges are shown in Figure 4.2-16. The costs presented in these figures do not include the costs associated with energy or capacity penalties.

Table 4.2-14 shows the capital investment and annualized costs of the operating lime FGD systems in the United States. These costs are escalated to reflect mid-1979 dollars.

4.2.3.2 The Limestone FGD Process--

The limestone and the lime FGD processes are similar in many aspects. In the limestone process, limestone slurry is used as the absorbent, as is lime slurry in the lime process. The use of limestone, however, requires different feed preparation equipment than is used in preparing lime slurries and also necessitates other process differences; the limestone process, for example, requires a higher liquid to gas (L/G) ratio because the absorbent is less reactive than lime. The exact L/G required is a function of SO_2 removal required, the inlet SO_2 gas stream concentration, the absorbent inlet pH, and other items. Even with such differences, the processes are so

TABLE 4.2-12. SENSITIVITY ANALYSIS OF A
500-MW LIME FGD SYSTEM
CAPITAL INVESTMENT[97]

	Percent of total direct cost		
	Individual cost	Subtotal for module	Total
Lime preparation			
Conveyors	1.4		
Slakers and pumps	0.4		
Storage silos	3.0		
Storage tanks	0.7		
Pumps and motors	0.1		
		5.6	
SO_2 scrubbing			
Absorbers	39.9		
Fans and motors	5.1		
Heat exchangers (reheaters)	7.8		
Soot blowers	3.0		
Valves and ducting	4.1		
Hold tanks	2.6		
Pumps and motors	7.5		
		70.0	
Sludge disposal			
Clarifiers	2.5		
Chemical storage	0.1		
Mobile equipment	0.2		
Tanks and agitators	0.2		
Pumps and motors	0.6		
		3.6	
Total installed cost			79.2
Raw material inventory		0.8	
Sludge pond		20.0	
Total direct costs			100.0
Total indirect costs			38.3
Contingencies		27.7	
Contractor fees		8.3	
Land cost		0.4	
Total capital investment			174.7

TABLE 4.2-13. SENSITIVITY ANALYSIS OF A 500-MW LIME FGD SYSTEM ANNUALIZED COSTS[97]

	Percent of total annualized cost		
	Individual cost	Subtotal	Total
Operation and maintenance			
Lime	11.4		
Sludge fixation chemicals	1.9		
Water	0.1		
Electricity	6.7		
Reheat	1.8		
Direct labor	1.0		
Supervision	0.1		
Maintenance labor	10.2		
Maintenance supplies	1.5		
Plant overheads	6.4		
Payroll overheads	0.2		
Sludge handling	1.9		
		43.2	
Fixed charges		56.8	
Total annualized costs			100.0

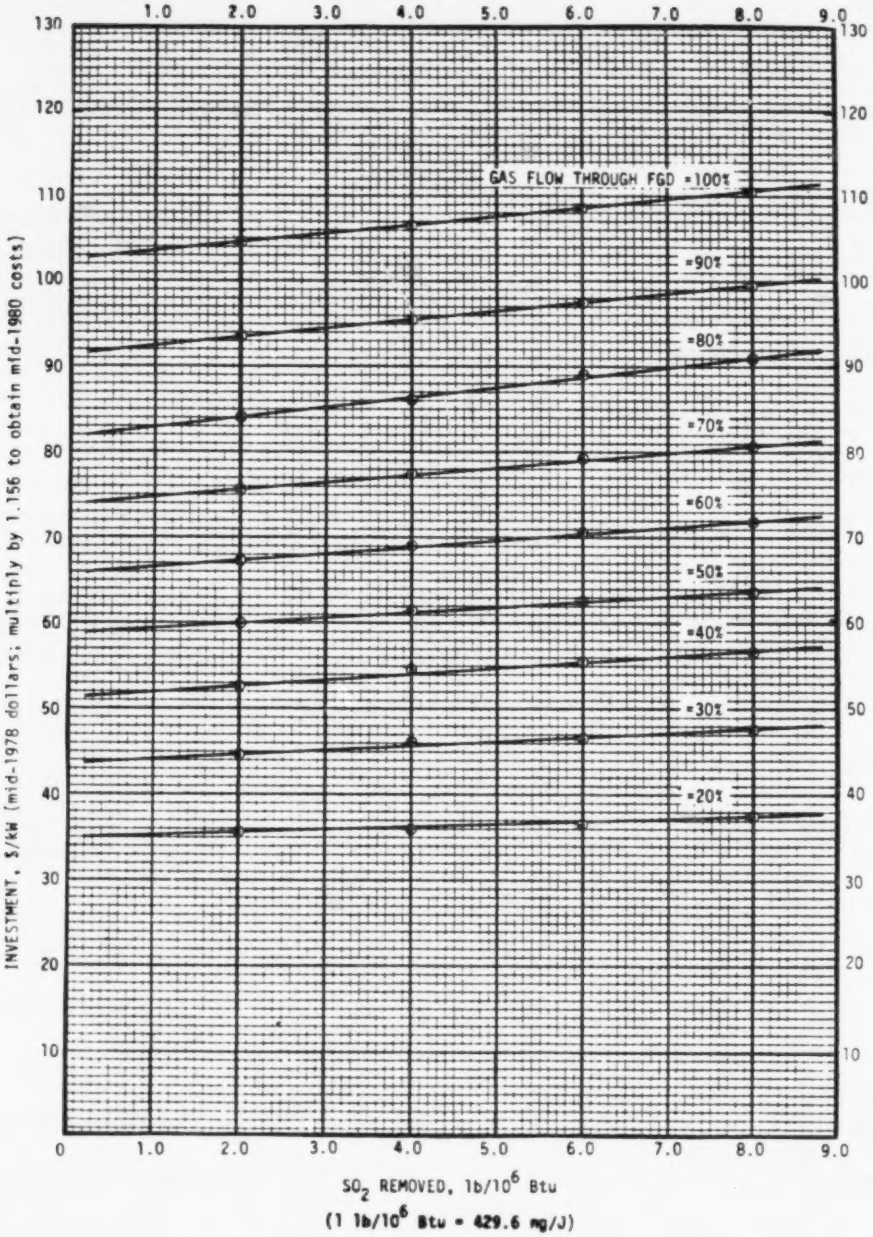

Figure 4.2-13. Capital investment excluding cost of sludge pond and land for a lime FGD system at a bituminous-coal-fired 500-MW plant.[98]

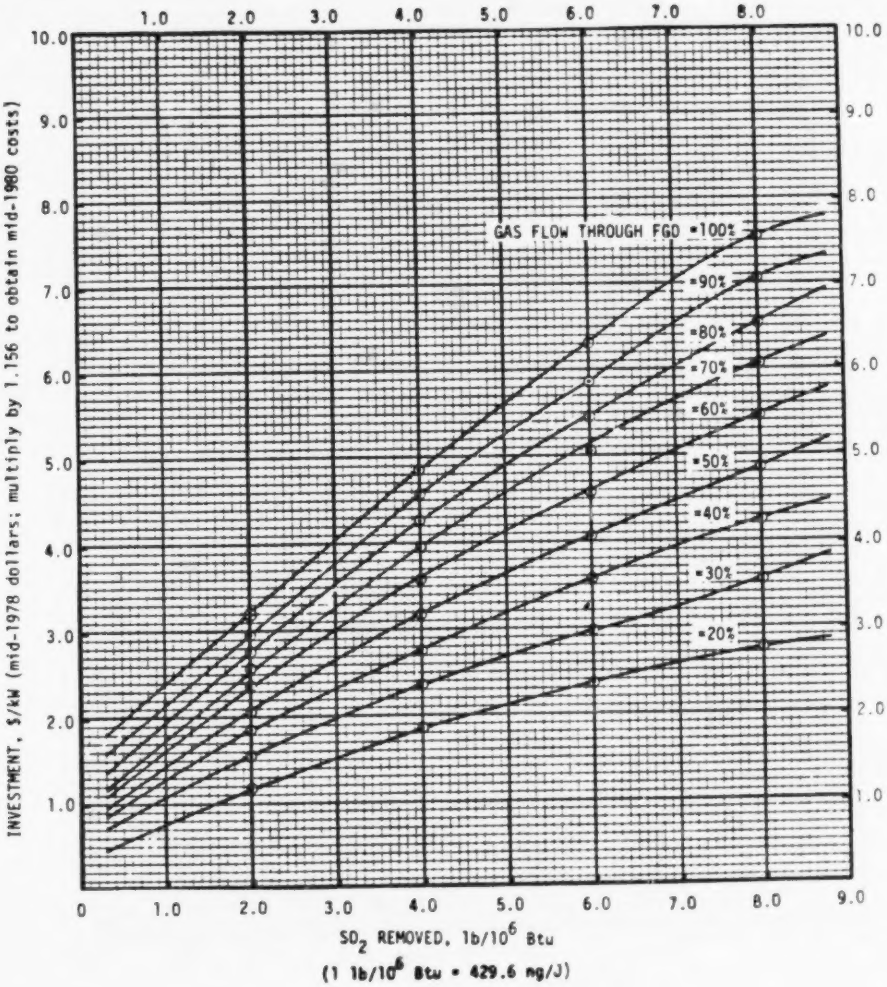

Figure 4.2-14. Capital cost of sludge pond and land for a lime FGD system at a bituminous-coal-fired 500-MW plant.[99]

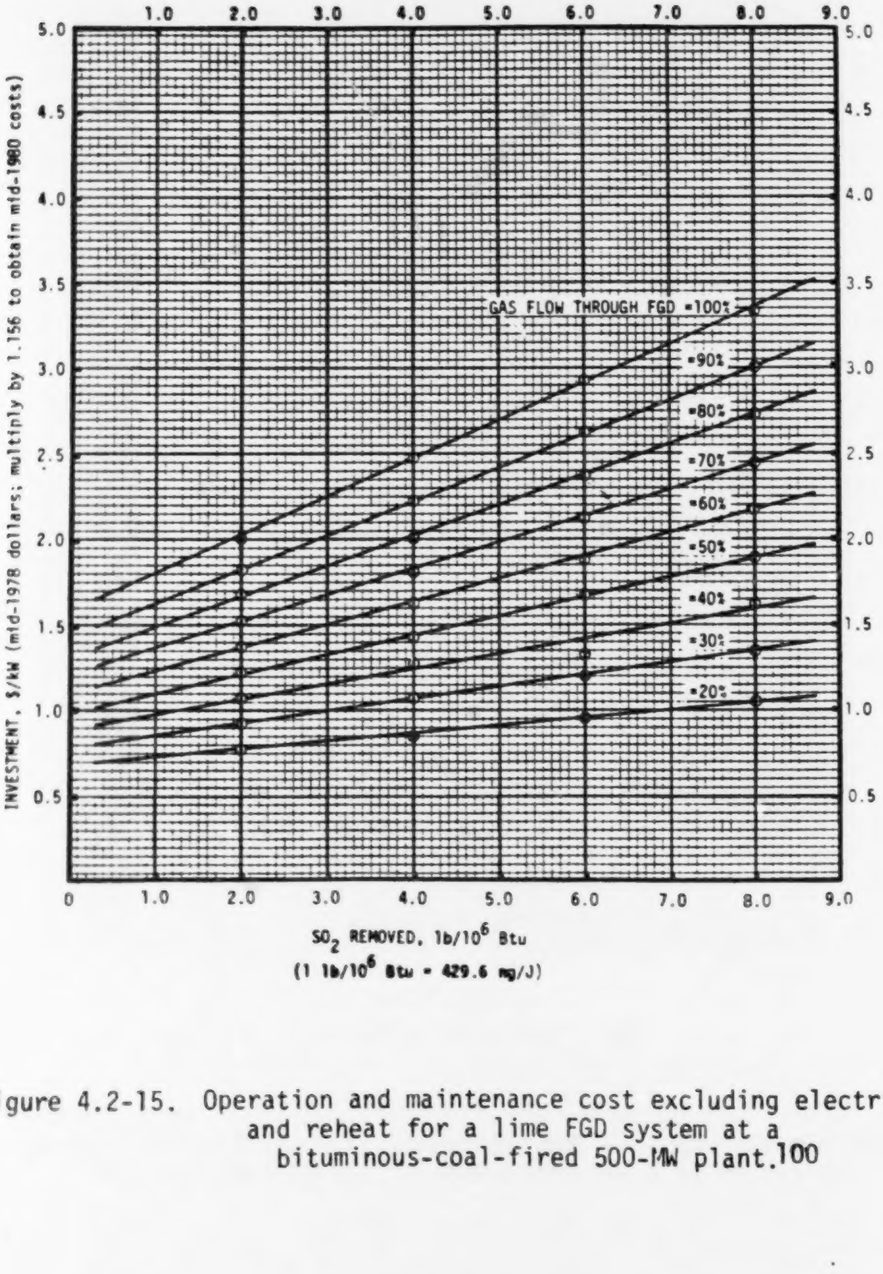

Figure 4.2-15. Operation and maintenance cost excluding electricity and reheat for a lime FGD system at a bituminous-coal-fired 500-MW plant.[100]

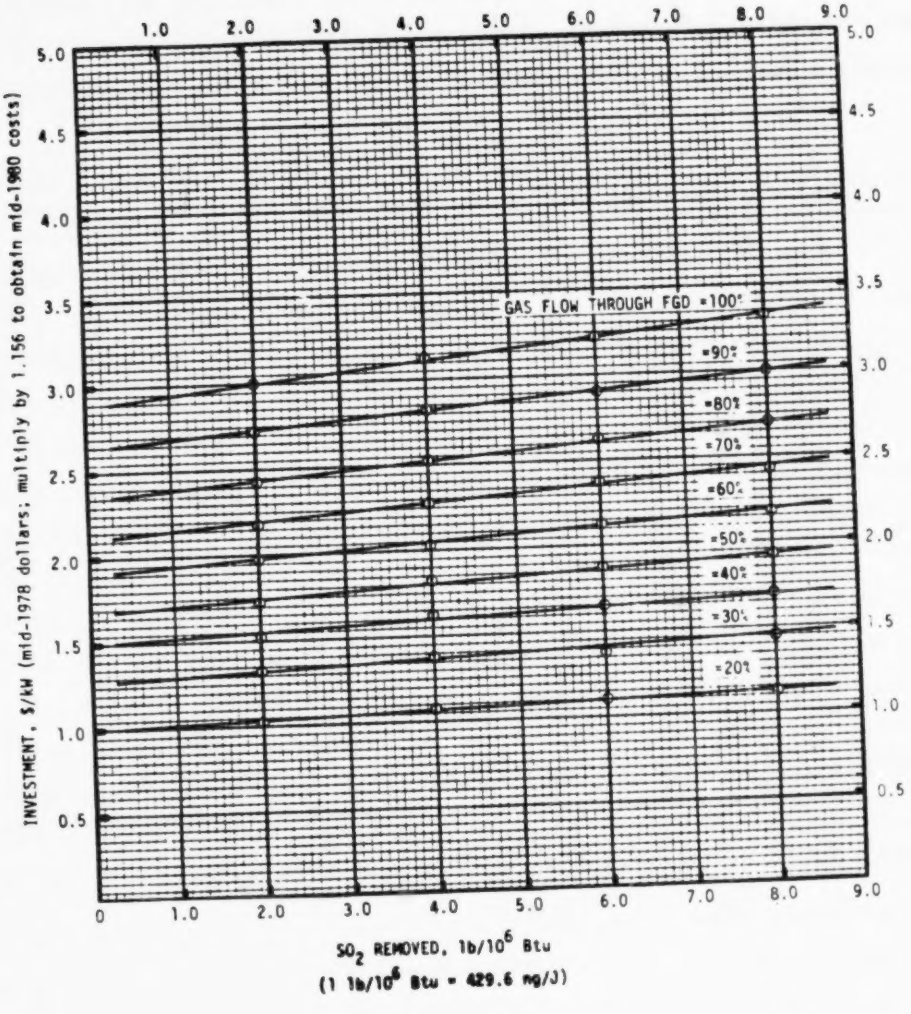

Figure 4.2-16. Fixed charges for a lime FGD system at a bituminous-coal-fired 500-MW plant.101

TABLE 4.2-14. CAPITAL AND ANNUALIZED COSTS OF OPERATIONAL LIME FGD SYSTEMS[97]

Station-unit(s)	System capacity, MW	Adjusted costs (mid-1979) Capital cost, \$/kW	Annualized cost, mills/kWh	Design SO_2 removal, %
Conesville 5	400	81.88	8.58	89.5
Elrama 1-4	570	147.10	9.03	83
Phillips 1-6	410	162.60	9.91	83
Hawthorn 3-4	200	100.96	5.03	70
Green River 1-3	64	89.74	6.06	80
Cane Run 4	178	93.21	6.68	85
Cane Run 5	183	78.06	6.43	85
Paddys Run 6	65	88.47	7.53	90
Colstrip 1-2	720	89.40	4.70	60
Bruce Mansfield 1-2	1650	119.00	10.04	92.1

similar that it is possible to design a system that can use either lime or limestone as the absorbent.

Process chemistry--The chemistry of the limestone process differs from that of the lime process only in the way that the calcium ion becomes available for absorption of SO_2; calcium ion generation in the limestone process takes place according to the following reactions:

$$(1)\quad CaCO_3(s) \rightarrow CaCO_3\,(aq)$$

$$(2)\quad CaCO_3\,(aq) \rightarrow Ca^{++} + CO_3^{=}$$

Other reactions are the same as those in the lime process.

The SO_2 in the flue gas stream contacts water forming the sulfite ion, which reacts with the calcium ion to yield insoluble calcium sulfite hemihydrate or gypsum, as shown in Reactions 7, 8, and 9 in the lime process description.

The quantities of limestone required and the volume of sludge generated may be calculated from the chemical reactions. With the assumption of 95 percent limestone purity and a 1.3 molar stoichiometric ratio, the requirement is 1.37 weight units of limestone per weight unit of SO_2 removed.

The sludge from a limestone process consists of calcium sulfite hemihydrate, calcium carbonate, gypsum, limestone impurities, and any excess unreacted limestone. The exact proportions of calcium sulfite hemihydrate and gypsum depend on such factors as inlet SO_2 content, excess oxygen, and absorbent pH. Because the FGD sludge is always an aqueous slurry, the weight of the associated water must be included in the total sludge weight.

System description[102]--Most of the equipment in a limestone FGD system is similar to that in a lime-based system. The major difference is in feed and slurry preparation. In a limestone system, the feed generally must undergo size reduction before the slurry is prepared; although preground rock of less than 200-mesh particle size can be purchased and used directly for slurry preparation, this is rarely done because of the high cost. Therefore, a limestone FGD system generally incorporates equipment for size reduction.

The raw limestone can be stored in open piles without protection from weather. Because it can be stored in the open and because it is cheaper than lime, large inventories can be maintained.

The SO_2 removal efficiency of the system is dependent on the limestone stoichiometry up to a certain level; after this level is achieved, no increase in SO_2 removal is obtained with an increase in the limestone stoichiometry.

Unclassified byproduct limestone from quarries may be an ideal feed. The unclassified crushed stone contains a high percentage of fines, and although it requires special handling equipment, this limestone splits readily along bedding planes, forming irregular, thin plates or blade-shaped pieces that interlock and chip easily into fine particles.

Wet ball mills at the FGD installations grind the raw limestone feed to the size suitable for slurry preparation. The crushed limestone slurry from the ball mill is sent to a classifier, from which the larger-size particles are fed back to the ball mill for regrinding.

The description of the lime FGD system in Section 4.2.3.1 is applicable to the limestone system except that the feed preparation modules are different because of the difference in the properties of the two feed materials. Other aspects of the system as well as the types of scrubber/absorber are essentially similar.

Figure 4.2-17 is a diagram of a typical limestone FGD system. Individual systems may deviate from that shown, depending upon plant characteristics and the system supplier.

Because limestone is less reactive than lime, some of the process parameters are different. The L/G ratio of a limestone system is higher, and the residence time in process tanks is longer than that of the lime system. Typical L/G ratios for limestone FGD systems using spray tower absorbers often are in the 8 to 11 liters/m^3 (60 to 80 gal/1000 acf) range. Spray absorbers are the most common in limestone systems. The design of scrubbing module equipment also requires a consideration of limestone reactivity.[103]

The configuration and design of a reaction tank affect the chemistry of limestone dissolution. A plug-flow reaction tank designed to prevent the

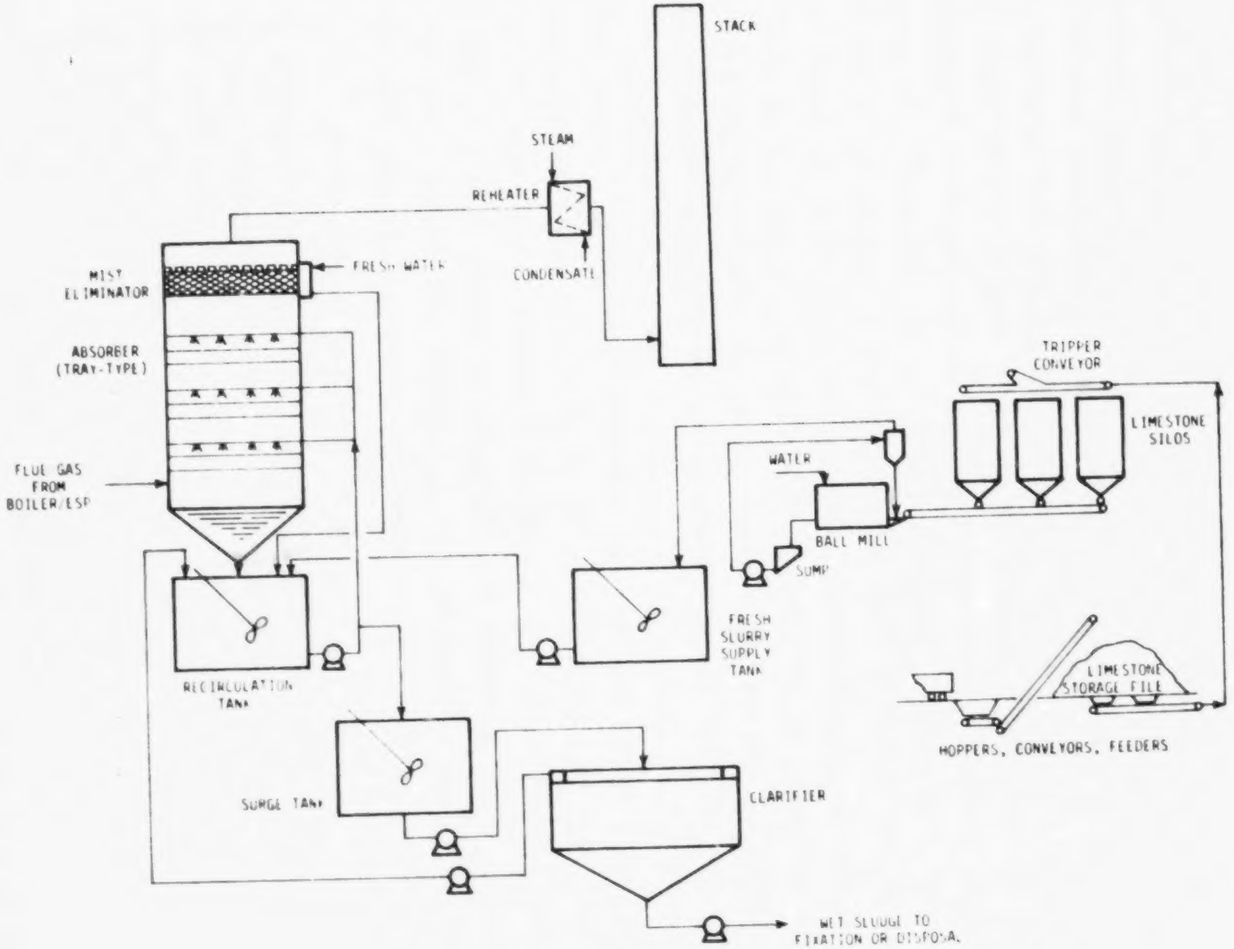
STACK
STEAM
REHEATER
CONDENSATE
MIST ELIMINATOR
FRESH WATER
ABSORBER (TRAY-TYPE)
FLUE GAS FROM BOILER/ESP
RECIRCULATION TANK
TRIPPER CONVEYOR
LIMESTONE SILOS
WATER
BALL MILL
SUMP
FRESH SLURRY SUPPLY TANK
LIMESTONE STORAGE PILE
HOPPERS, CONVEYORS, FEEDERS
SURGE TANK
CLARIFIER
WET SLUDGE TO FIXATION OR DISPOSAL

Figure 4.2-17. Diagram of a typical limestone FGD system.

backmixing of the reacting stream is reported to yield significant improvements in limestone utilization and in SO_2 removal.[104] This plug-flow design apparently drives the additive dissolution reaction further toward completion and makes more liquid-phase alkalinity available for reaction with sorbed SO_2.[104,105]

In design of the scrubber/absorber for a limestone system, pH of the circulating slurry must be considered. A low pH leads to better limestone utilization but reduces SO_2 removal efficiency. The scrubber should be designed for optimum SO_2 removal. Some proposed designs take advantage of the flexibility afforded by operating multiple stages at different pH levels. Borgwardt reports 97 percent limestone utilization with 81 percent SO_2 removal in a two-stage, forced-oxidation, pilot system.[106] A low-pH liquor contacts the entering flue gas in an initial scrubbing stage, in which part of the SO_2 is removed and the limestone dissolution is essentially completed. High-pH liquor contacts the flue gas in the second stage, where additional SO_2 removal takes place. Blowdown liquor from the second stage is bled to the first stage. Makeup limestone slurry is added in the second-stage loop.

Another design that may enhance limestone utilization is the Weir scrubber. This is a multistage, crossflow scrubber, in which the lowest-pH liquor contacts the entering flue gas and the highest-pH liquor contacts the exiting flue gas. It is expected that this countercurrent flow arrangement will optimize limestone utilization and SO_2 removal efficiency. The Weir scrubber has not yet been tested in commercial limestone systems, but five are currently being installed.[107]

Operational status and current developments--As of the third quarter of 1979, limestone FGD represented 40 percent of the total committed capacity for utility FGD systems in the United States.[91] Figure 4.2-18 shows the growth of limestone capacity in the United States from 1968, as estimated through 1982; the figure includes the capacity growth trend for all the FGD systems combined.[108]

Efforts to improve efficiency and other process areas of the lime and limestone systems are carried on simultaneously, and usually a new development in either process is applicable to both.

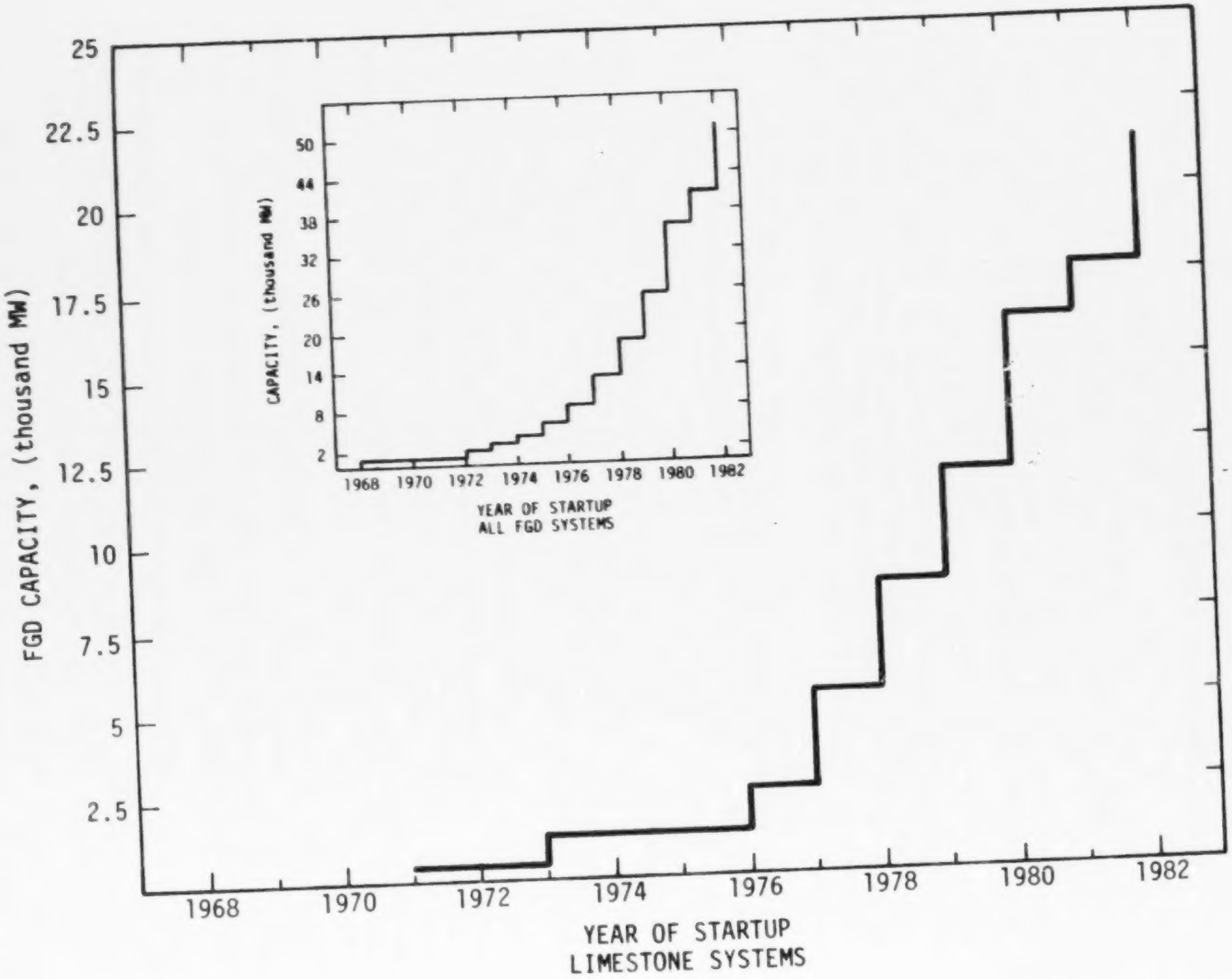

Figure 4.2-18. Actual and projected growth of limestone and other U.S. FGD capacity.[108]

Current listings of operational limestone FGD systems are given in the EPA Utility FGD Survey (published quarterly) and the EPA Industrial FGD Survey (published semiannually). Operating problems and successes are well documented in these publications.

Some additional operating histories for limestone FGD systems are as follows:[109]

- At the Mohave 170-MW facility of the Southern California Edison Co., SO_2 removal efficiencies in excess of 95 percent were reported for a Turbulent Contact Absorber using limestone slurry for a low-sulfur coal application.
- At the Martin Lake Station of Texas Utilities Generating Company, SO_2 removal efficiency of 99 percent with 90 to 92 percent limestone utilization is reported for the FGD system on Unit 1. The 99 percent removal was achieved using wetted film contactors; the efficiency dropped to 80 to 85 percent without using wetted contactors.[110]
- Reports on the packed-bed module at the 115-MW Cholla facility show 92-percent removal of sulfur dioxide using limestone slurry scrubbing.
- The 10-MW test facility at the TVA Shawnee has reported SO_2 removal efficiencies in excess of 90 percent. During one run in February 1976, efficiency reached 96 percent in the TCA unit on a high-sulfur coal application.
- The initial operating performance of the Widows Creek No. 8 550-MW scrubber facility indicates that SO_2 removal efficiencies substantially higher than the designed 75 percent value have been measured. SO_2 removal efficiencies in the range of 85 to 94 percent were reported during the period of November 1977 through February 1978.[111]
- During the St. Clair No. 6 limestone scrubbing demonstration and test program conducted by Detroit Edison and Peabody, SO_2 removal values of 90 and 91 percent (90 percent design) were measured on high (3.0 percent) and low (0.4 percent) sulfur coals.
- At the 167-MW Will County No. 1 facility of the Commonwealth Edison Co., SO_2 removal efficiencies as high as 86.8 percent were measured during a high-sulfur coal (4.0 percent) burn program, which yielded inlet SO_2 loadings averaging 3573 ppm.
- SO_2 removal efficiencies in excess of 90 percent have been measured in tests conducted by Combustion Engineering and Kansas Power and Light at Lawrence, Unit No. 4, in 1977. The testing was conducted on the recently installed rod scrubber and spray tower

absorber system, which replaced the original limestone injection and scrubbing system (1968 startup). Actual efficiencies in the 95.5 to 97.5 percent range were measured for low-sulfur (0.55 percent) coal.

Some additional information on several systems of particular interest are as follows:

- The Unit No. 1 steam generator of the La Cygne Power Station of Kansas City Power and Light is a 820-MW (net) system that has one of the earliest limestone scrubber systems installed in the United States (1973). The sulfur content of the coal ranges from 5 to 6 percent. Despite the problems at startup, the availability of the system improved steadily.

  This system was designed for 76 percent SO_2 removal efficiency. Actual SO_2 efficiency has been 80.18 percent with the seven modules operating at 720 MW. Under maximum load, the removal efficiency averaged 76.2 percent.[112,113]

- The No. 1 and No. 2 units of the Sherburne County Station of Northern States Power Co. have a net capacity of 700 MW each and burn 0.8 percent sulfur coal. Availabiliy for Unit No. 1 averaged 85 percent for the 4 months of operation after startup. During one 12-month period, availability was in excess of 90 percent. Unit No. 2 has shown even better startup performance, with operabilities averaging about 95 percent for the first 4 months. For the first 8 months of operation of No. 1 unit, the SO_2 removal efficiency was 50 to 55 percent, which was sufficient to meet local regulations.[112,113]

Based on the operating experience of limestone systems, there is evidence from individual SO_2 removal test runs to show that limestone FGD systems can operate at 90 percent SO_2 removal or greater and that they can operate reliably (90 percent operability) with proper design and maintenance on both low- and high-sulfur coals.[114,115]

System costs--The capital cost of a limestone FGD system is higher than that of a comparable lime FGD system. This higher cost is attributable to the additional limestone preparation equipment and to the larger sludge processing system necessitated by the higher sludge generation rate of the limestone process.

Table 4.2-15 lists the costs of limestone and lime FGD systems installed on units burning Eastern coals with sulfur contents of 3.5 percent and 7.0 percent.[116] The FGD systems are designed to comply with a 516 ng/J (1.2 lb/million Btu) SO_2 emission limitation.

TABLE 4.2-15. COSTS OF LIMESTONE AND LIME FGD SYSTEMS[116]

Coal type and system capacity		Capital costs			Annualized costs		
		Lime, $/kW	Limestone, $/kW	Differential, %	Lime, mills/kWh	Limestone, mills/kWh	Differential, %
Eastern, 3.5% S	200 MW	174.46	202.46	16.0	11.65	12.87	10.5
	500 MW	124.93	142.58	14.1	8.91	9.38	5.3
	1000 MW	103.71	119.02	14.8	7.48	8.04	7.5
Eastern, 7.0% S	200 MW	217.36	252.11	16.0	15.09	16.37	8.5
	500 MW	156.34	185.94	18.9	11.54	12.52	8.5
	1000 MW	131.59	156.53	19.0	10.07	10.82	7.4

Table 4.2-16 shows the capital investment and annualized costs of several operational utility limestone FGD systems in the United States.[96] These costs are escalated to reflect mid-1979 dollars.

To help put the costs given in these two tables into perspective, the following items should be known:

- The FGD systems in Table 4.2-15 include spare absorber modules and equipment redundancy, not found in some older FGD systems, to help assure greater reliability of operation.
- Also the systems in Table 4.2-15 were designed to meet 90 percent SO_2 removal.
- For coal of about 3.5 percent sulfur, the capital costs in both tables are close.
- For FGD systems designed to meet SO_2 removal requirements lower than 90 percent, the cost is reduced.
- The annualized costs reflect the higher capital cost of the units in Table 4.2-15. Capital costs are often a major portion of annualized costs.

Energy and environmental impacts--Because the limestone and lime FGD processes are similar, the energy and environmental impacts are also similar. Although there may be minor quantitative differences in the sludge quantities and energy requirements, these are not significant. A secondary energy impact of lime systems is the energy required in the lime calcining operation, which is normally achieved outside of the utility. The energy consumption for various lime processes ranges from 4.7 to 6.4 GJ/Mg (4 to 5.5 million Btu/ton) of lime.[117]

The discussion of energy and environmental impacts in Section 4.2.3.1 is generally applicable to the limestone system.

4.2.3.3 Double Alkali Process--

Several FGD processes may be classified as double or dual alkali systems. Basically, double alkali scrubbing is an indirect lime/limestone process that removes SO_2 from exhaust gases, which avoids some of the plugging and scaling associated with direct lime/limestone scrubbing. The process normally involves absorption of SO_2 in a sodium solution in the absorber followed by regeneration of the absorbent in a separate system

TABLE 4.2-16. CAPITAL AND ANNUALIZED COSTS OF OPERATIONAL LIMESTONE FGD SYSTEMS[96]

Station and unit No.	System type	System capacity, MW	Coal sulfur content, %	Adjusted costs (mid-1979)		SO_2 design removal efficiency, %
				Capital cost, $/kW	Annualized cost, mills/kWh	
Cholla 1	Retrofit	115	0.5	64.76	2.98	92
Petersburg 3	New	530	3.3	116.34	7.59	85
La Cygne 1	New	820	5.4	78.64	4.37	80
Sherburne 1 - 2	New	1420	0.8	83.15	3.20	50
Winyah 2	New	280	1.7	76.90	3.38	69
Southwest 1	New	200	3.5	136.11	7.14	80
Widows Creek 8	Retrofit	550	4.3	130.91	6.11	80

through reaction with a calcium-based alkaline slurry. Regenerated absorbent is recycled to the absorption loop; the calcium sulfites and sulfates are precipitated and discarded.

Process chemistry-- The alkaline solution used to absorb SO_2 may be a solution of either potassium, sodium, or ammonia compounds. In the United States, the scrubbing liquor is generally a sodium salt solution.

The basic absorbent is formed by addition of soda ash (sodium carbonate) or caustic (sodium hydroxide) to water. Several sodium species are available for reaction with the SO_2, including sodium carbonate, sodium hydroxide, and sodium sulfite. The primary products of reaction include sodium sulfite and sodium bisulfite. Following are the main absorption reactions:[118-119]

(1) $2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$

(2) $Na_2 CO_3 + SO_2 \rightarrow Na_2SO_3 + CO_2 \uparrow$

(3) $Na_2SO_3 + SO_2 + H_2O \rightleftarrows 2NaHSO_3$

(4) $NaOH + SO_2 \rightarrow NaHSO_3$

Also some of the SO_3 present in the exhaust stream may react with sodium hydroxide to form sodium sulfate as follows:

(5) $2NaOH + SO_3 \rightarrow Na_2SO_4 + H_2O$

In the absorber, and through the rest of the system to a lesser degree, some sulfite is oxidized as follows:

(6) $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

The sulfate species is inactive and is unavailable for further SO_2 removal. The extent of oxidation is a function of the oxygen and SO_2 content of the flue gas, the temperature of the gas in the absorption vessel, and the design of the absorber. As an example, the typical excess air level in high-sulfur, coal-fired utility boilers leads to oxidation levels of 10 to 15 percent of the SO_2 removed.

After absorption of SO_2, spent absorbing liquor is bled to the regeneration system and reacted with either lime or limestone. The reactions vary, depending upon which reactant is used. Regeneration with slaked lime (calcium hydroxide) takes place over several stages. The calcium hydroxide reacts with sodium bisulfite, sodium sulfite, and sodium sulfate in the following series of reactions:[120-122]

$$(7)\quad 2NaHSO_3 + Ca(OH)_2 \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2H_2O \downarrow + 3/2H_2O$$

$$(8)\quad Na_2SO_3 + Ca(OH)_2 + 1/2H_2O \rightarrow 2NaOH + CaSO_3 \cdot 1/2H_2O \downarrow$$

$$(9)\quad Na_2SO_4 + Ca(OH)_2 + 2H_2O \rightarrow 2NaOH + CaSO_4 \cdot 2H_2O \downarrow$$

The precipitated calcium species (sulfite and sulfate) are separated from regenerated liquor.

Regeneration with limestone (calcium carbonate) involves the following main reaction:[123]

$$(10)\quad CaCO_3 + 2NaHSO_3 + 1/2H_2O \rightarrow Na_2SO_3 + CaSO_3 \cdot 1/2H_2O \downarrow + CO_2 \uparrow + H_2O$$

The bisulfite is the main reactive species, because the sulfite ion is not sufficiently acidic to react with limestone.[124]

At present limestone regeneration is not in commercial use, although several laboratory studies have been conducted. Therefore, the emphasis in this section is on lime regeneration.

After removal of the calcium sulfite and sulfate species from the regenerated scrubbing liquor, two additional steps may be required. The first step, needed in all cases, involves the addition of makeup sodium to replace the small amount of sodium lost in the waste solids. The sodium is usually added as sodium carbonate or sodium hydroxide. The second step involves reduction of the calcium ion concentration in the scrubbing liquor to prevent scaling in the scrubber. This step is not always needed if the calcium concentration in the return liquor is low. If excess calcium is present, however, the solution must be softened by addition of sodium carbonate as the makeup sodium. Calcium is removed by the following reaction:[125]

$$(11)\quad Na_2CO_3 + Ca^{++} \rightarrow CaCO_3 \downarrow + 2\ Na^{+}$$

Sodium carbonate must sometimes be added in amounts greater than the makeup requirement to soften the solution sufficiently.

A residence time of about 1 to 4 seconds in an absorber is necessary for SO_2 absorption. To achieve maximum SO_2 removal with an optimum amount of energy input, various absorber types are used by the industry, the most common of which are the tray tower or packed tower types. Typically the L/G ratio is 1.3 to 2.0 liters/m^3 (10 to 15 gal/1000 acf), the pressure drop is 1.5 to 3.0 kPa (6 to 12 in. H_2O), and the spent absorbent pH is 6.0.[126]

The sludge generated by the double alkali process is essentially the same as that generated by lime scrubbing (Section 4.2.3.1) and is handled in the same way. The presence of soluble sodium compounds in sludge from the double alkali system may necessitate more care in disposal to prevent leaching or runoff of sodium species.

Operational status and current development--Several vendors offer variations of the double alkali system. In the United States, all double alkali systems use a sodium salt as the absorbent and lime as the regenerant. The system offers high SO_2 removal capabilities and minimizes scaling and plugging.

Several successful bench-scale, pilot plant and prototype double alkali FGD systems have been tested on boiler flue gas applications in the United States. The success of these programs resulted in commitments by three separate electric utility companies to install full-scale double alkali FGD systems on coal-fired boilers. Two of the new utility double alkali systems began operation in early 1979, and the third came onstream in late 1979. In addition, several systems are working on coal-fired industrial boilers, and one pilot plant system and one prototype have been tested on utility units.

At the end of 1979, double alkali FGD systems comprised about 6 percent of the utility FGD capacity in operation. Applications on utility and industrial boilers are as follows:[127]

Company: Southern Indiana Gas and Electric
Plant: A.B. Brown 1 (New Plant)
Location: West Franklin, Indiana
Stream treated: Off-gas from coal-fired boilers
System size: 265-MW
SO_2 inlet: 2810 ppm (4.5 percent sulfur coal)
Startup date: March 1979

Company: Louisville Gas and Electric
Plant: Cane Run 6 (Retrofit system)
Location: Louisville, Kentucky
Stream treated: Off-gas from coal-fired boilers
System size: 288-MW (Net)
SO_2 inlet: 3471 ppm (4.8 percent sulfur coal)
Startup date: April 1979

Company: Central Illinois Public Service
Plant: Newton 1 (New plant)
Location:
Stream treated: Off-gas from coal-fired boilers
System size: 575-MW (Net)
SO_2 inlet: -- (4 percent sulfur coal)
Startup date: November 1979

Company: Caterpillar Tractor Company
Plant: Joliet Plant
Location: Joliet, Illinois
Stream treated: Off-gas from coal-fired boilers
System size: 48.8 m^3/s (103,500 acfm) (18-MW)
SO_2 inlet: 2300 ppm (4 percent sulfur coal)
Startup date: September 1974

Company: Firestone Tire and Rubber Company
Plant: Pottstown Plant
Location: Pottstown, Pennsylvania
Stream treated: Off-gas from oil-fired boiler
System size: 6.6 m^3/s (14,000 acfm)
SO_2 inlet: 1,000 ppm
Startup date: January 1975

Company: Caterpillar Tractor Company
Plant: Mossville Plant
Location: Mossville, Illinois
Stream treated: Off-gas from 4 coal-fired boilers
System size: 113 m^3/s (240,000 acfm) (57-MW)
Fuel properties: Coal, 3.2 percent sulfur average
Startup date: October 1975

Company: General Motors, Inc.
Plant: Chevrolet Parma
Location: Parma, Ohio
Stream treated: Off-gas from coal-fired boilers
System size: 124 m^3/s (262,000 acfm) (32 MW)
SO_2 inlet: 800 to 1300 ppm (1.5 to 3.0 percent sulfur coal)
Startup date: March 1974

One prototype and one pilot plant double alkali system have operated on utility coal-fired boilers:[128]

Utility: Utah Power and Light Company
Unit: Gadsby Station, Unit No. 3
Location: Gadsby, Utah
Unit size: 1.2 m^3/s (2500 acfm) (0.6 MW)
Fuel properties: Coal, 0.4 percent sulfur average
Startup date: 1971
Note: Terminated 1973

Utility: Gulf Power Company
Unit: Scholz, Unit No. 1
Location: Chattahoochee, Florida
Unit size: 35 m^3/s (75,000 acfm) (20-MW)
Fuel properties: Coal, 3 to 5 percent sulfur
Startup date: February 1975
Note: Terminated July 1976

As a result of the success of pilot and prototype systems, three full-scale double alkali systems are in operation on coal-fired utility boilers. Utility operating results are sketchy because initial operations are still in progress.

The GM Parma system has performed well with regard to SO_2 removal. Results of a 1-week test in 1974 indicate SO_2 removal efficiencies in the 94- to 99-percent range, with relatively low inlet SO_2 levels (600 to 1200 ppm) and high excess air rates. A test was conducted by A.D. Little, Inc., and General Motors (GM) from August 19, 1974 to May 14, 1976. It consisted of three 1-month intensive test periods and 18 months of lower-level tests. Removal of SO_2 reflects the variations in operating modes employed by GM during the period, but removal efficiencies were at 90 percent for the viable operating modes. Operation during April and May 1976 was excellent and A.D. Little, Inc., recommended continued operation in the mode used during this period.[129]

The operability (hours the FGD system was operated per boiler operating hours in a period expressed as a percentage) of the Parma system for the 1-year period from May 1976 through April 1977 was about 70 percent. The system's best period of operation was May through August 1976, when operability averaged 94 percent.[129] The GM Parma plant has several unique characteristics that affect operability. Each boiler is equipped with its own separate scrubbing module with no provisions for crossflow between modules. The GM plant is a developmental system, and as such is subject to modifications. Many of the low operability periods were due to mechanical outages or outages for modifications to accommodate and test new modes of operation. Several different operating modes have been investigated, and significant improvements have been obtained in both process and mechanical performance. It is believed that in the latest operational mode the system is capable of long-term reliability.

The Joliet system has achieved excellent SO_2 removal efficiencies of between 85 and 95 percent under various operating conditions. Sulfur dioxide inlet concentrations are high, about 2300 ppm. The system was designed to attain an emission level of 860 ng/J (1.9 lb $SO_2/10^6$ Btu) (75 percent SO_2 removal), but has consistently performed much better than designed.[130]

The operability of the FGD system has been improving steadily. Process availability for the period October 24, 1975, through June 1976 has been 100 percent. Most problems at the Joliet plant are mechanical; the majority are solved while still on stream or during scheduled shutdowns. As a consequence, there have been few forced outages.[130]

The Firestone-Pottstown system has exhibited excellent SO_2 removal efficiencies of 90 percent on high-sulfur oil, but no data are available for its performance on coal. It has also achieved a very high availability: 99 percent for the first 12 months of operation. Most downtime periods were due to mechanical component failure or to maintenance, and not to unwanted chemical changes or side reactions. No scaling problems have been experienced.[131]

The Gadsby scrubbing system has performed well with respect to SO_2 removal. Various modes of operation were tested using two types of absorbers. With the polysphere absorber, SO_2 removals of 90 percent were achieved, giving outlet concentrations of 15 to 40 ppm SO_2. With the venturi absorber, efficiencies ranged from 80 to 85 percent SO_2 removal.[131]

With the exception of the first 3-month operating period, during which some gypsum scaling problems were encountered, dilute mode operations were conducted for almost 2 years without any major problems. No operating problems causing shutdown were experienced between October 1972 and August

1974. For convenience, the system was shut down on weekends, but no drainage of solution or cleaning of equipment took place during these shutdowns.[131]

The Gulf Power Company, Scholz plant prototype system started up February 3, 1975, and operated continuously through July 18, 1975, when it was shut down for repairs and modifications. The second period of operation was from September 16, 1975, through January 2, 1976.

The system exhibited excellent SO_2 removal capabilities of 90 percent and greater. Using the combined venturi/tray tower absorber configuration at a venturi liquor pH above 5.2, outlet SO_2 concentrations below 50 ppm were achieved, which corresponds to greater than 95-percent removal. Raising the pH of the venturi liquor above 6.0 resulted in SO_2 removal efficiencies greater than 98 percent.[131,132]

The Scholz plant was designed to demonstrate the viability of the double alkali process technology for application on utility coal-fired boilers. As such, this prototype plant had less spare equipment than would be normal in full-scale applications. The operability of the system has been steadily improved; during 4 months of operation, it was 94 percent.[132]

The operability of double alkali FGD systems on coal-fired industrial boilers and prototype utility installations has been improved. Most operability problems were due to design-related equipment shortcomings in these prototype installations. It should be pointed out that most installations did not have spare equipment; however, this is included in full-scale utility systems.[132]

The vendors of double alkali systems have developed confidence in their reliability: as evidenced by guarantees of 90-percent availability for the first year of operation and 100 percent for the life of the plant (based on a boiler operating rate of 70 percent for some of the new, full-scale utility applications). The systems are all guaranteed to achieve 85 to 95 percent SO_2 removal efficiency on high-sulfur coal applications. No new low-sulfur coal applications are planned, but similar guarantees would be expected for such systems.[133]

Corrosion, erosion, and scaling problems have not been important factors at double alkali FGD installations. Full-scale versions of these systems are not expected to experience these problems either. The double alkali system has demonstrated the ability to perform well under fluctuating SO_2 inlet concentrations. At the Scholz plant, the design inlet SO_2 concentration was 1800 ppm. At inlet concentrations varying from 800 to 1700 ppm, removal efficiencies were above 90 percent.[133]

Energy and environmental impacts--Operation of a double alkali FGD system requires relatively little energy. There may be some potential adverse environmental effects, but none significantly more consequential than from other types of FGD systems.

The electrical requirement is variable, usually in a range of 1 to 2 percent of the energy output of the boiler.[134] The reheating requirement is usually about 2 percent of the energy output of the boiler for about 50°F of reheat.[134] The concepts of energy and capacity penalties are discussed more fully in Section 4.2.3.1.

Beneficial environmental impacts are the prime reason for operating the scrubber. Sulfur dioxide removal efficiencies of 95 percent are achievable with current technologies in both high-sulfur and low-sulfur coal applications.[134,135] A potential adverse effect is emission of sulfurous and sulfuric acid mist if the flue gas stream is not processed to remove the entrained liquor. The principal adverse impacts, however, are due mainly to the generation of sludge.

At a 1000-MW plant burning 3.5 percent sulfur coal with 14 percent ash, 90 percent SO_2 removal would generate about 210,000 Mg (232,000 tons) of dry sludge per year.[51] This plant would consume about 2,152,000 Mg (2,373,000 tons) of coal and generate about 201,000 Mg (222,000 tons) of ash per year.[51] The potential environmental effects of sludge are discussed in detail in Section 4.2.3.1. Because the double alkali sludge contains soluble sodium compounds, care must be taken to reduce leachage or runoff. This can be achieved most often by constructing a plastic- or clay-lined sludge impoundment and managing the placement of waste and/or by chemically treating to fix the waste.

System costs--Little cost information is available on the early double alkali system applications, but some is reported for the large coal-fired utility applications. Table 4.2-17 presents cost data on the three utility double alkali systems, adjusted to July 1, 1979 dollars.[136] Two of the systems were recently completed, and the third should be on line in late 1979.

TABLE 4.2-17. CAPITAL AND ANNUALIZED COSTS OF UTILITY DOUBLE ALKALI FGD SYSTEMS[136]

Station, unit	Capacity, MW	Adjusted costs (mid-1979)	
		Capital costs, $/kW	Annualized costs, mills/kWh
Cane Run 6	277	72.7	4.8
A.B. Brown 1	250	61.4	3.5

Generic cost data on double alkali FGD systems have been developed in support of the NSPS for utility boilers. These data are presented in graphical form in Figures 4.2-19 and 4.2-20.[137] The values are higher than those presented in Table 4.2-17, but they represent costs for systems with spare scrubbing trains and a high level of installed spare capacity.

4.2.3.4 Nonregenerable Sodium-Based Flue Gas Desulfurization--

Nonregenerable sodium-based FGD systems utilize a clear liquor absorbent (soluble salts) that minimizes the plugging, scaling, and erosion that are common in some calcium-based scrubbing systems. Solutions of sodium hydroxide or sodium carbonate are currently being used to scrub SO_x from flue gases.

Nonregenerable sodium-based scrubbing systems are well developed and widely applied on industrial boilers. Whereas about 90 percent of utility FGD systems treat flue gases with lime or limestone absorbent, sodium-based scrubbing technology accounts for about the same percentage (93 operating systems) in the industrial sector.[138]

Nonregenerable sodium-based scrubbing is based on the following reactions (assuming the presence of an absorber recirculation loop):

(1) $Na_2SO_3 + SO_2 + H_2O \rightarrow 2NaHSO_3$

(2a) $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + CO_2 + H_2O$

(2b) $NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O$

(3) $2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$

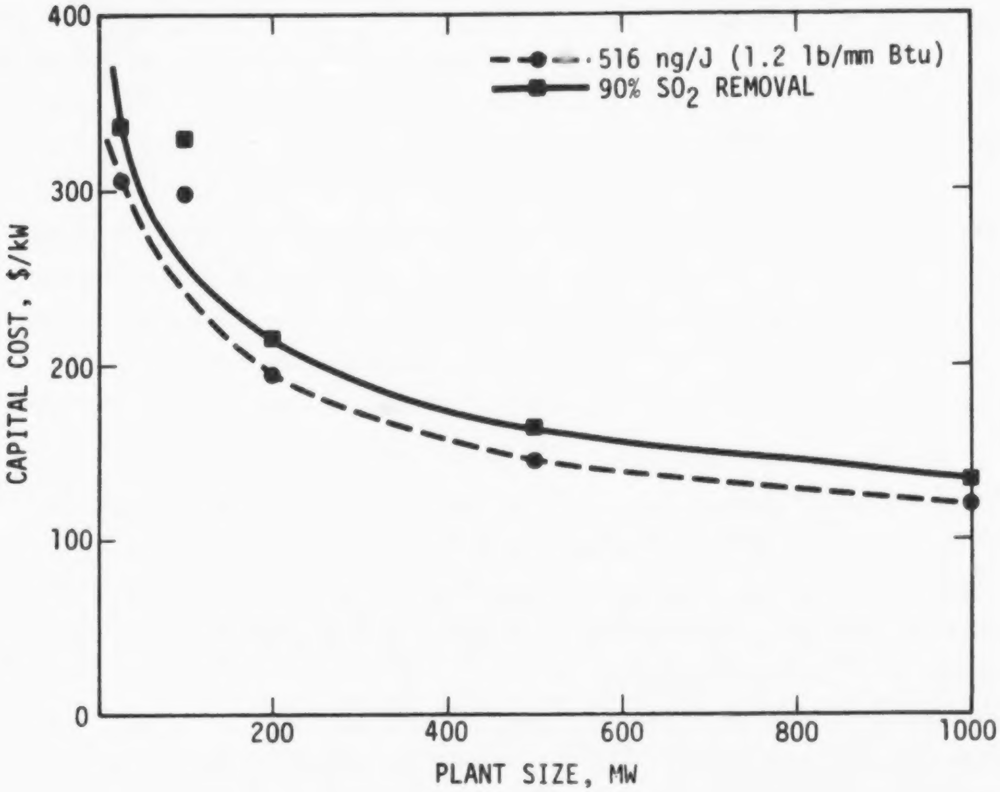

Figure 4.2-19. Capital cost of a double alkali FGD system on a boiler firing 3.5 percent sulfur coal.[137]

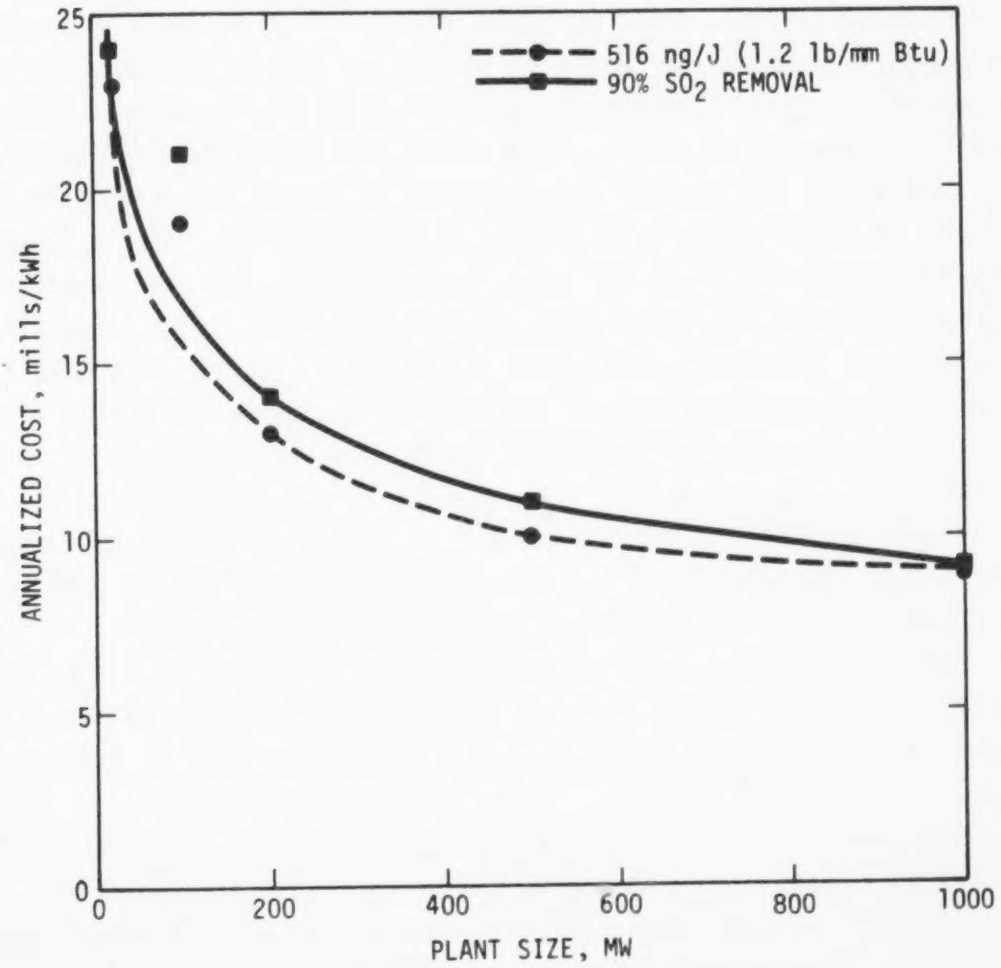

Figure 4.2-20. Annualized costs of a double alkali FGD system on a boiler firing 3.5 percent sulfur coal.[137]

Reaction 2a occurs in a sodium carbonate (Na_2CO_3) scrubbing system, and Reaction 2b is the primary reaction in sodium hydroxide (NaOH) scrubbing systems. Reaction 3 is common to both types of systems. Reaction 1 accounts for the main SO_2 removal in both systems.

If fly ash is not collected concurrently with the SO_2 absorption, a nonregenerable sodium scrubbing system produces only a liquid waste stream. Typically, a bleed stream from a recirculation loop is discharged at a rate equivalent in sulfur content to that at which SO_2 is being absorbed.[139] Total dissolved solids in the waste stream are approximately 5 percent.[140] The stream may or may not be processed to remove the sodium bisulfite (product of Reaction 1) or to oxidize the sulfite to sulfate to reduce the chemical oxygen demand of the waste stream. Small industrial units may be able to discharge the waste stream directly into treatment equipment. If treatment is necessary, vapor compression distillation, multistage flash evaporation, or reverse osmosis may be used to reduce the amount of total dissolved solids (TDS);[140] however, this is not currently done to great extent.

Figure 4.2-21 is a basic process flow diagram of a typical nonregenerable sodium FGD system. The chemistry of sodium scrubbing dictates the basic components of the system, but many variations occur.

Sodium carbonate, a solid, is often stored in onsite silos, whereas sodium hydroxide, usually received in liquid form, is stored in onsite tanks. Both absorbents are highly soluble and are used in aqueous solutions.

Some coal-fired units utilize electrostatic precipitators or fabric filters to remove fly ash from the flue gases before they enter the scrubbing system. In such cases, the SO_2 absorber can be a tray-type tower or spray tower, which provides good scrubbing efficiency at low pressure drops. Oil-fired units present a similar situation. For simultaneous particulate matter removal and SO_2 absorption, venturi scrubbers have been used. Following cleanup, the gas passes through mist eliminators and often is reheated before being exhausted to the atmosphere.

Because the sodium-based liquor is highly reactive, it is possible to use liquid-to-gas ratios (L/G) as low as 0.668 liter per actual cubic meter

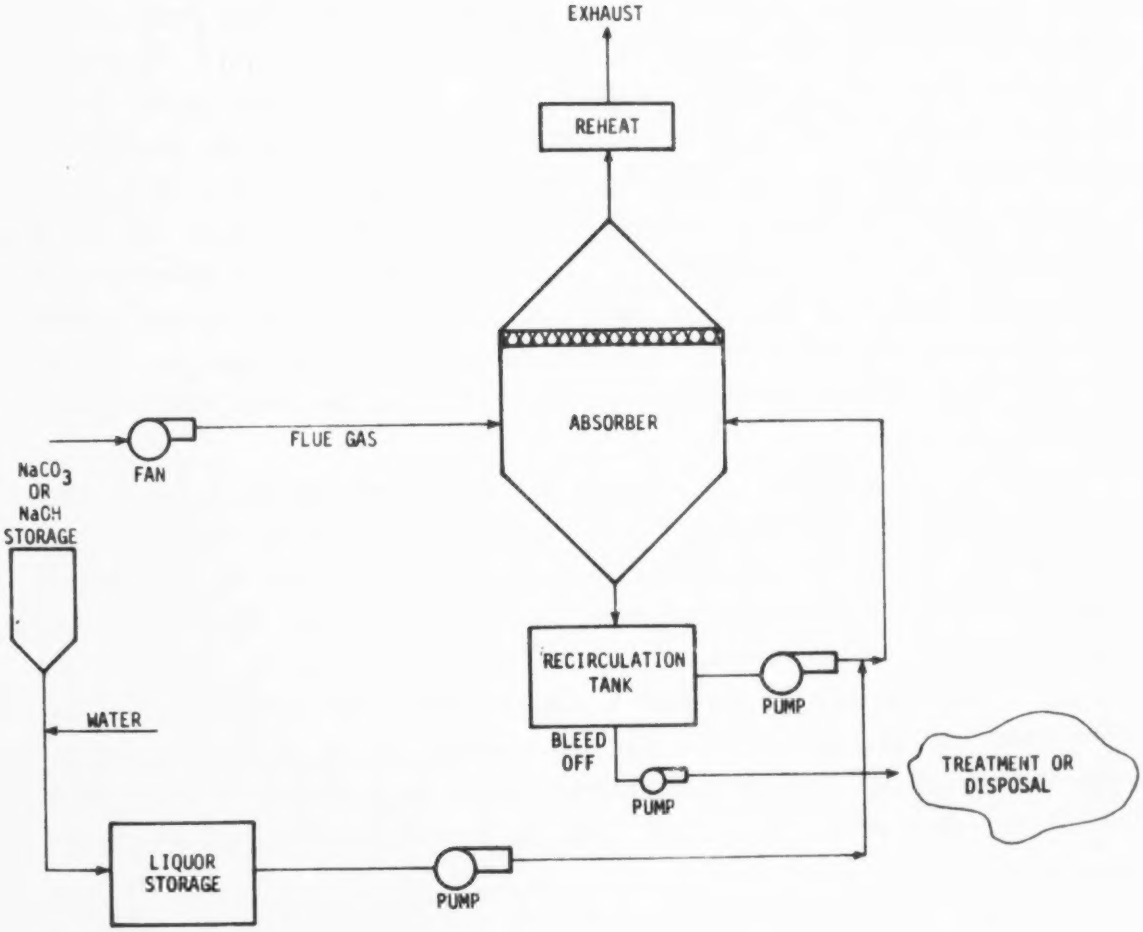
EXHAUST
REHEAT
ABSORBER
FLUE GAS
FAN
NaCO3
OR
NaCH
STORAGE
WATER
RECIRCULATION
TANK
PUMP
BLEED
OFF
PUMP
TREATMENT OR
DISPOSAL
LIQUOR
STORAGE
PUMP

Figure 4.2-21. Basic nonregenerable sodium FGD system.

of gas (5 gallons per 1000 actual cubic feet). This high reactivity also permits rapid response of the system to loading changes. The liquor feed rate is usually controlled by adjusting the pH at the absorber inlet or outlet. Spent sodium sulfite solution is usually removed by bleeding the recirculation loop.[141]

The only nonregenerable sodium-based FGD systems in operation at utility plants are at the Reid Gardner Power Station of Nevada Power Company and at Jim Bridger Unit 4 of Pacific Power & Light. A simplified process flow diagram of the FGD systems on Units 1, 2, and 3 is shown in Figure 4.2-22.[142] This figure shows several differences from the basic system discussed earlier. The source of sodium at the Reid Gardner Station is trona, a low-grade ore containing 60 percent sodium carbonate, 20 percent sodium chloride, 10 percent insolubles, and 10 percent sulfates and inert dissolved solids. From storage in onsite silos, the trona is conveyed to a slurry tank, where the absorbent is dissolved. The solution is then pumped to a clarifier, in which the insoluble impurities are allowed to settle. The clarified sodium carbonate solution is injected into the venturi recirculation loop.

Hot flue gas from the boiler first passes through mechanical collectors for primary particulate removal (75 percent). After passing through a fan, the flue gas is ducted into two streams, which enter twin throat venturi scrubbers, where the gas is quenched. The scrubbed gas then enters the droplet separator tower, where the finer droplets coalesce on the wall, and the gas rises and bubbles through a single sieve tray flooded with clear water from the ash pond. More SO_2 is absorbed on the sieve tray, after which the gas passes through a horizontal radial-vane-type mist eliminator. The gas is reheated before exhaust, both to enhance buoyancy and to prevent condensation in the stack.

Blowdown from the venturi recycle tank may be mixed with the alkaline clarifier underflow stream in the postneutralization tank. Spent liquor is sent to the ash settling pond, and pond overflow is pumped to an evaporation pond.[143]

Industrial applications of nonregenerable sodium-based scrubbing are much more widespread than in the utility industry. In fact, some 90 percent

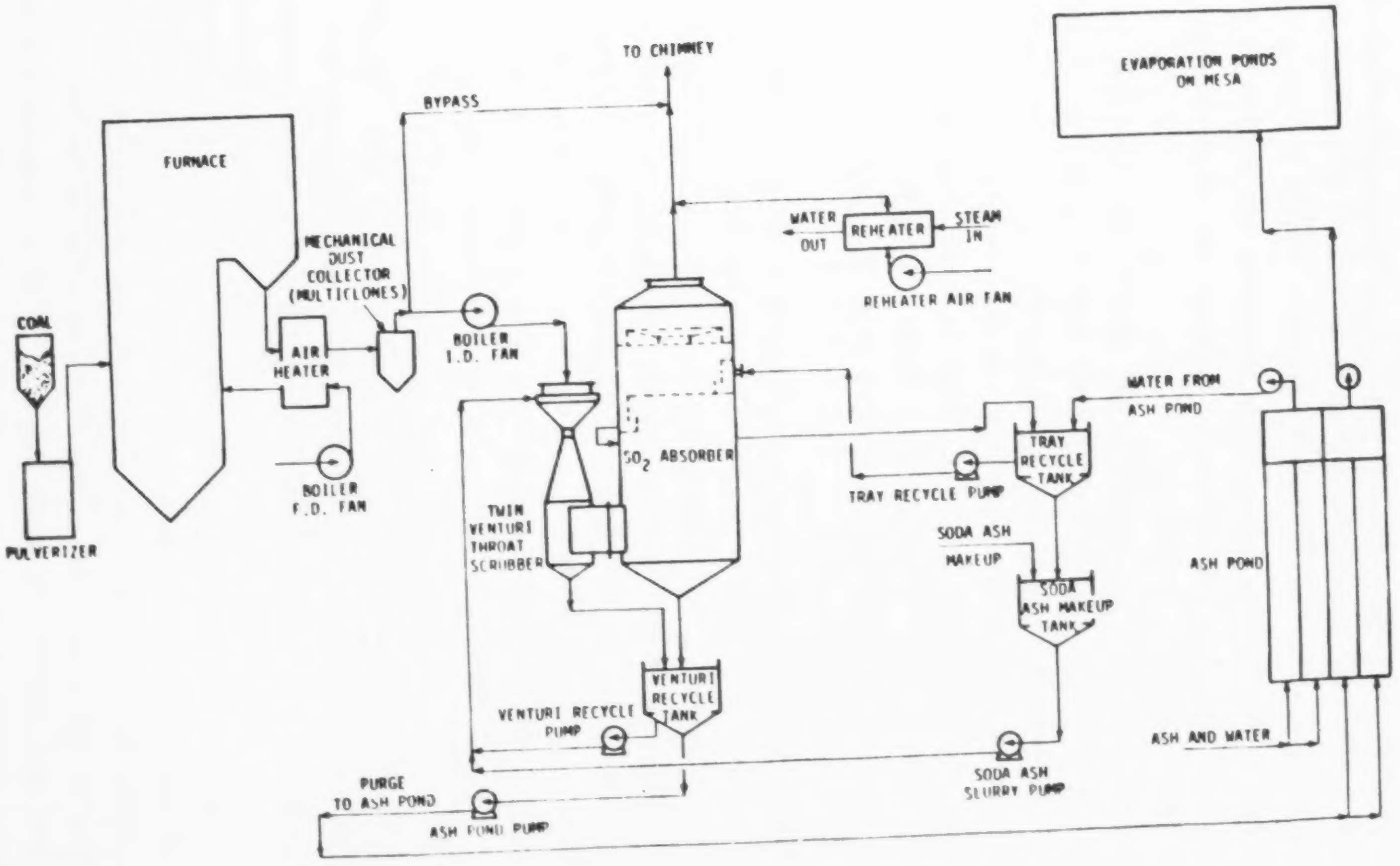
TO CHIMNEY
BYPASS
FURNACE
EVAPORATION PONDS ON MESA
MECHANICAL DUST COLLECTOR (MULTICLONES)
COAL
AIR HEATER
BOILER I.D. FAN
BOILER F.D. FAN
PULVERIZER
WATER OUT
REHEATER
STEAM IN
REHEATER AIR FAN
SO_2 ABSORBER
TWIN VENTURI THROAT SCRUBBER
WATER FROM ASH POND
TRAY RECYCLE TANK
TRAY RECYCLE PUMP
SODA ASH MAKEUP
SODA ASH MAKEUP TANK
ASH POND
ASH AND WATER
VENTURI RECYCLE TANK
VENTURI RECYCLE PUMP
SODA ASH SLURRY PUMP
PURGE TO ASH POND
ASH POND PUMP

Figure 4.2-22. Process diagram of an FGD system, Nevada Power Co., Reid Gardner Station.[142]

of the industrial FGD applications use nonregenerable sodium-based scrubbing. At present, 93 nonregenerable sodium-based FGD systems are treating flue gases from 158 industrial boilers. Capacities range from 18,900 to 386,350 Nm^3/h (12,000 to 245,000 scfm, 6 MW to 123 MW), and systems are being offered by at least 14 different vendors. Sodium hydroxide is used as the reagent in 79 of the systems; the remainder use sodium carbonate.[144] Table 4.2-18 lists the industrial applications of nonregenerable sodium-based FGD technology.[145]

These applications in the industrial sector have been highly successful. The users regularly report excellent operating system reliabilities. The major advantage of the sodium-based systems is that SO_2 absorption by soluble sodium salts eliminates the scaling and plugging that occur in many calcium-based FGD systems.[146] In addition to the lower maintenance costs that result from scale-free operation, other attractive features of nonregenerable sodium-based systems are relatively low power requirements and high SO_2 collection efficiency.[147]

Although operating problems are relatively less frequent and less severe in the sodium-based FGD systems than in calcium-based systems, operation is not flawless. Inadequate control of FGD system pH is of concern, because effective pH control is essential to maximizing absorbent usage. Other mechanical problems, not peculiar to the nonregenerable sodium scrubbing systems, include failure of dampers and liners, pump problems, and inefficiency of mist eliminators. At the coal-fired installations, operators face the problems usually associated with fly ash (abrasion, erosion, and plugging).

Operational status and current developments--The three Nevada Power nonregenerable, sodium-based FGD systems have been operated well over a period of 5 years. Although the expected mechanical problems have occurred, the availability and operability of the FGD systems on the three units have exceeded 90 percent for extended periods.[148],[149]

The 18 industrial locations, which use the 93 FGD systems, have similar operating histories: problems have occurred, but the systems operate well the majority of the time. As a case in point, the sodium-based system at Alyeska Pipeline Service Company operated 1 year (second quarter 1978 through first quarter 1979) at 100 percent availability.[150] Chevron U.S.A.,

TABLE 4.2-18. INDUSTRIAL SITES USING NONREGENERABLE SODIUM FGD TECHNOLOGY[145]

Company	Location	Fuel	Flow rate,		Reagent	Vendor	SO_2 removal, %	Type system
			Nm³/h	(scfm)				
Alyeska Pipeline Service Co.	Valdez, Alaska	Oil	78,850	(50,000)	Sodium hydroxide	FMC Env. Equipment	96+	New
Belridge Oil Co.	McKittrick, Calif.	Oil	18,900	(12,000)	Sodium hydroxide	Heater Technology	90	New
Belridge Oil Co.	McKittrick, Calif.	Oil	18,900	(12,000)	Sodium hydroxide	Thermotics, Inc.	90	New
Chevron U.S.A., Inc.	Bakersfield, Calif.	Oil	391,100	(248,000)	Sodium carbonate	Koch Engineering	90	Retrofit
FMC (Soda Ash Plant)	Green River, Wy.	Coal	703,350	(446,000)	Sodium carbonate	FMC Env. Equipment	95	New
General Motors Corp.	Dayton, Ohio	Coal	56,750	(36,000)	Sodium hydroxide	Entoleter, Inc.	86	Retrofit
General Motors Corp.	Pontiac, Mich.	Coal	169,200	(107,300)	Sodium hydroxide	GM Environmental	N.A.	New
General Motors Corp.	St. Louis, Mo.	Coal	100,950	(64,000)	Sodium hydroxide	A.D. Little	90+	Retrofit
General Motors Corp.	Tonowanda, N.Y.	Coal	145,100	(92,000)	Sodium hydroxide	FMC Env. Equipment	90-95	Retrofit
Getty Oil Co.	Bakersfield, Calif.	Oil	113,500	(72,000)	Sodium carbonate	FMC Env. Equipment	90+	Retrofit
Getty Oil Co.	Bakersfield, Calif.	Oil	149,800	(95,000)	Sodium carbonate	In-house design	96	Retrofit
ITT Rayonier, Inc.	Fernandina Beach, Fla.	Bark & Oil	277,550	(176,000)	Sodium hydroxide	Airpol Industries	80-85	Retrofit
Kerr-McGee Chemical Corp.	Trona, Calif.	Coke, Coal & Oil	772,750	(490,000)	Sodium carbonate	Combustion Equipment Assoc.	98+	New
Mead Paperboard Co.	Stephenson, Ala.	Oil	157,700	(100,000)	Sodium carbonate	Airpol Industries	95	New
Mobil Oil Co.	San Ardo, Calif.	Oil	276,000	(175,000)	Sodium hydroxide	In-house design	90	Retrofit
Northern Ohio Sugar Co.	Freemont, Ohio	Coal	63,100	(40,000)	Sodium hydroxide	In-house design	N.A.	Retrofit
Texaco, Inc.	San Ardo, Calif.	Oil	599,250	(380,000)	Sodium hydroxide	Ceilcote	73	Retrofit
Texasgulf	Granger, Wy.	Coal	270,800	(140,000)	Sodium hydroxide	Swemco, Inc.	90	New

N.A. - Not available.

Inc., reports operability in excess of 95 percent since startup in July 1978.[151]

Cost--Although the reported costs of nonregenerable sodium FGD systems vary considerably, some general conclusions can be drawn. Dickerman reports[152] that the capital costs of nonregenerable sodium FGD systems are always lower than the costs of comparably sized double alkali, limestone, or Wellman-Lord systems. Sodium-based systems are less complex and require less equipment, largely because of the high solubility and reactivity of the sodium absorbent. High solubility and the consequent absence of slurry solids allow use of less exotic construction materials, and high reactivity allows use of simpler or smaller absorber vessels.

These characteristics of the sodium-based system, however, do not lead to comparable reductions in annual costs relative to other systems. The sodium absorbent is more expensive than lime and limestone and wastewater treatment may be required. Because of these cost items, the annual costs of a nonregenerable sodium-based FGD system rise more sharply with increasing unit size than do the annual costs of other FGD systems. Figures 4.2-23[153] and 4.2-24[154] show the capital and annual costs versus system size for several industrial-scale FGD processes capable of removing 90 percent of the SO_2 from flue gases generated by coal with 3.5 percent sulfur content. Table 4.2-19[155-157] presents costs of a nonregenerable sodium-based FGD system as reported by several utility and industrial operators. All costs are adjusted to mid-1979 dollars.

The PEDCo industrial cost data are derived from direct contact with the industrial FGD system users. Little or no redundancy is employed. Also the purged absorbent is often disposed of in municipal systems, deep wells, etc. Redundancy and an involved waste treatment ponding system can double the cost of the FGD system.

The utility cost numbers reflect the PEDCo utility FGD cost program (with redundancy and waste treatment costs built in) near the low end of its relevant range, based on the data used to prepare the program. The FMC costs are the estimates of a system vendor, which include little redundancy and waste treatment costs.

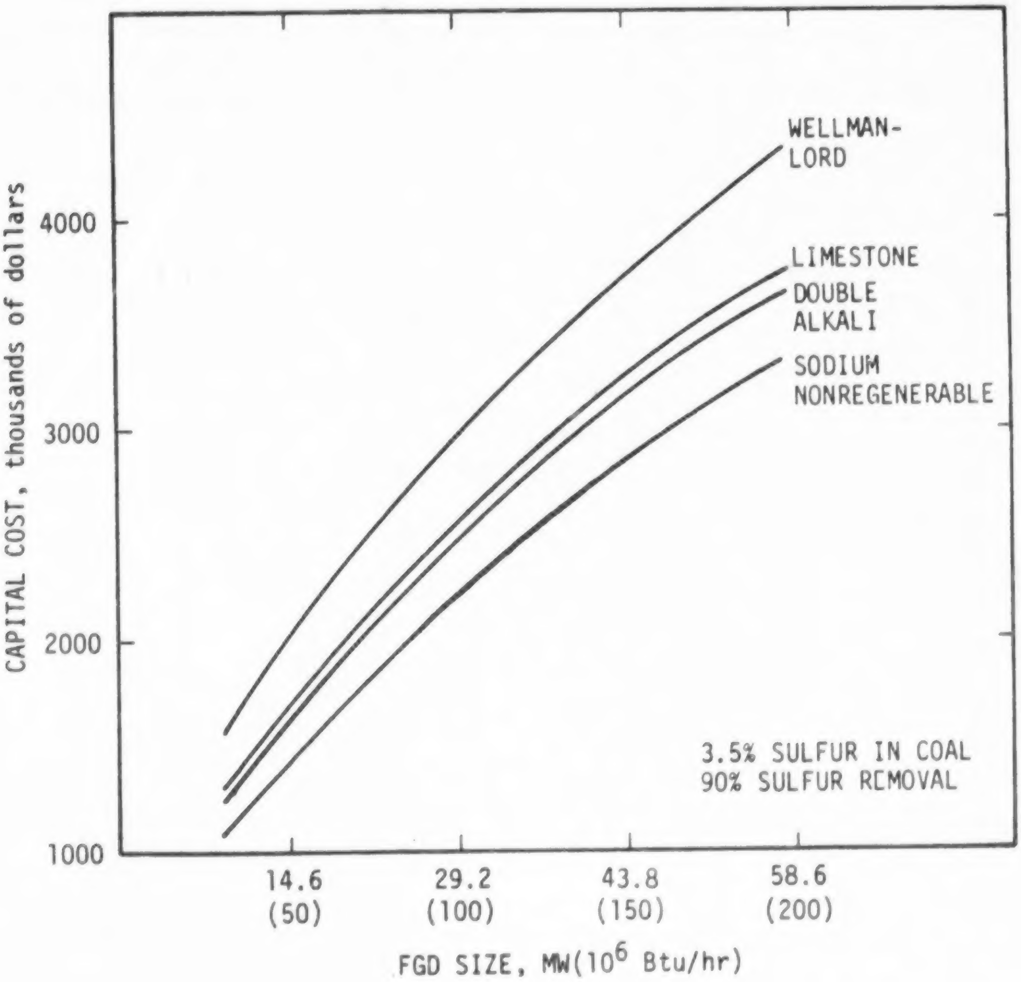

Figure 4.2-23. FGD capital costs versus unit size.[153]

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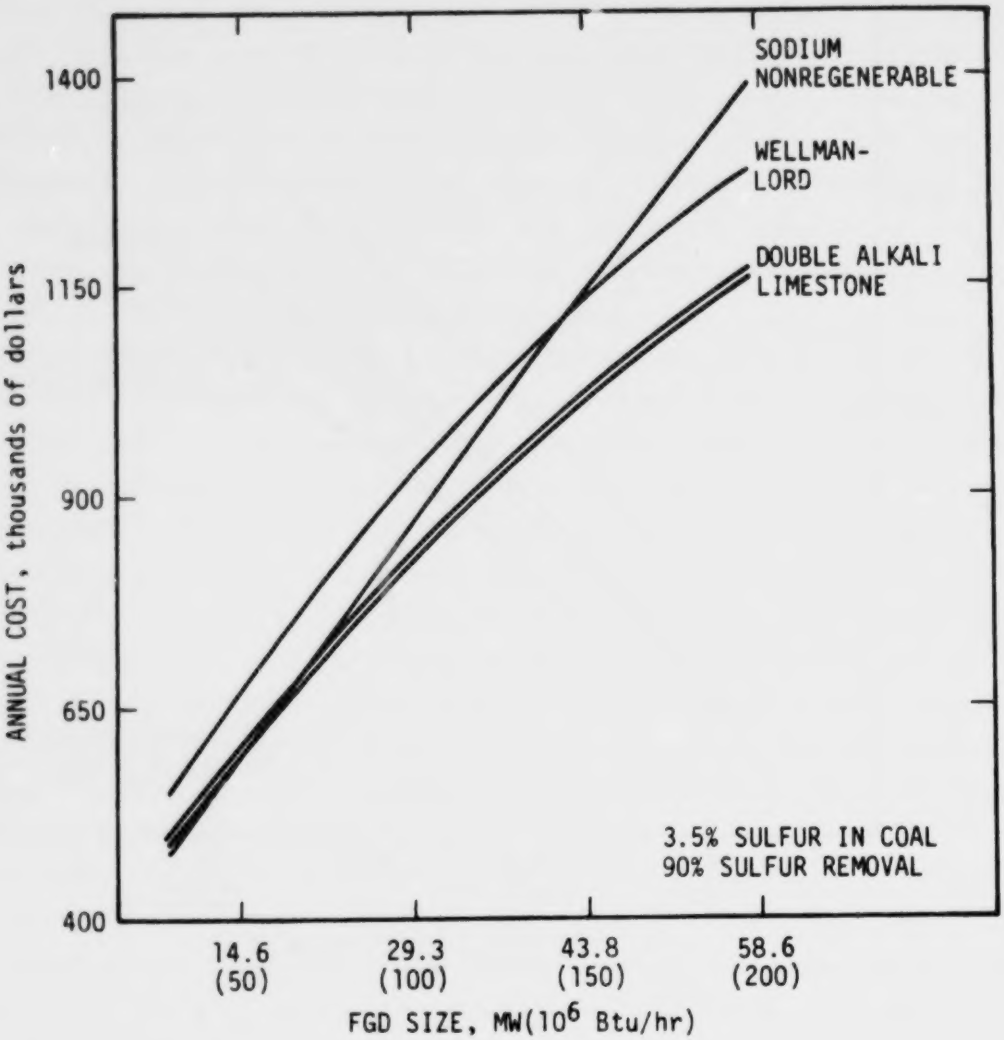


Figure 4.2-24. FGD annual costs versus unit size.[154]

TABLE 4.2-19. COSTS OF NONREGENERABLE SODIUM-BASED FGD SYSTEMS IN INDUSTRIAL AND UTILITY APPLICATIONS[a]

	Capital cost		Annual cost	
	Range	Average	Range	Average
Industrial				
PEDCo[155]	\$12.53-\$87.81/kW	\$33.33/kW	\$0.0839-\$0.2312/GJ (\$0.0885-\$0.2439/10^6Btu)	\$0.1578/GJ (\$0.1665/10^6Btu)
Radian[156]	\$56.31-\$95.89/kW	\$72.87/kW	\$0.82-\$1.35/GJ (\$0.86-\$1.42/10^6Btu)	\$1.01/GJ (\$1.07/10^6Btu)
Utility				
PEDCo[96]	\$71.02-\$120/kW	\$96.97/kW	3.73-5.11 mills/kWh	4.19 mills/kWh
FMC[157]	\$24.49-\$29.74/kW	\$27.12/kW	3.18-7.14 mills/kWh	5.05 mills/kWh

[a] The reported costs vary widely depending upon degree of redundancy and wastewater treatment.

Energy and environmental impact--The waste streams from the sodium-based nonregenerable systems consist of a solution of sodium sulfate and sulfite/ sulfate only if oxidation is employed. Current users of nonregenerable sodium alkali FGD systems dispose of the purge stream either by discharging it to onsite or municipal liquid waste treatment facilities or, in the West, by pumping it to large evaporative ponds, or injecting it in deep wells. As long as these means of disposal are feasible, the innate simplicity and high SO_2 removal capability of the system coupled with its low energy requirement make this system attractive at many sites.

Table 4.2-20[158] presents estimates of the liquid wastes from various size boilers firing different coals at the same removal efficiencies.

4.2.3.5 Ammonia-Based Process

In the ammonia-based wet SO_2 absorption process, flue gas from a stationary source is pretreated to remove most of the particulate matter (if necessary) by electrostatic precipitation, fabric filtration, or other means and is then water-quenched to its adiabatic saturation temperature. The conditioned, humid gas is brought into contact with an aqueous ammoniacal solution, which rapidly absorbs the SO_2. There are two basic ammonia-based processes, both with salable byproducts: a nonregenerable process with ammonium sulfate as byproduct and a regenerable process with elemental sulfur or sulfuric acid as byproduct. A nonregenerable process without oxidation would yield ammonium sulfite as byproduct.

Process chemistry--In a typical nonregenerable process with ammonium hydroxide as the feed liquor and ammonium sulfate as the byproduct, the following principal reactions occur:

SO_2 absorption:

$$(1)\quad 2NH_4OH + SO_2 \rightarrow (NH_4)_2SO_3 + H_2O$$

$$(2)\quad (NH_4)_2SO_3 + SO_2 + H_2O \rightarrow 2NH_4HSO_3$$

These reactions take place in the absorber during SO_2 absorption by ammoniacal solutions.

TABLE 4.2-20. WATER POLLUTION IMPACTS OF A NONREGENERABLE SODIUM SYSTEM[158]

Boiler size and type	Control level, %	3.5% S eastern coal		0.6% S western coal	
		liters/m^3	(gal/1000 acfm)	liters/m^3	(gal/1000 acfm)
8.8 MW (30 x 10^6 Btu/h) Underfeed stoker	90	50.7	(13.4)	10.2	(2.7)
	85	47.3	(12.5)	9.8	(2.6)
	75	42.4	(11.2)	9.1	(2.4)
	56	31.2	(8.4)		
22 MW (75 X 10^6 Btu/h) Chaingrate stoker	90	130.9	(34.6)	27.6	(7.3)
	75	106.4	(28.1)	22.3	(5.9)
	56	75.3	(19.9)		
44 MW (150 x 10^6 Btu/h) Spreader stoker	90	262.7	(69.4)	55.3	(14.6)
	75	211.6	(55.9)	44.7	(11.8)
	56	146.8	(38.8)		
58.6 MW (200 x 10^6 Btu/h) Pulverized coal	90	348.2	(92.0)	73.8	(19.5)
	85	315.6	(83.4)	66.6	(17.6)
	75	282.7	(74.7)	59.4	(15.7)
	56	200.2	(52.9)		
Avg. dissolved solid		Na_2SO_3 Na_2SO_4 Na_2CO_3	70 percent 18 percent 12 percent	Na_2SO_3 Na_2SO_4 Na_2CO_3	52 percent 35 percent 13 percent
Avg. TDS concentration, wt. %		5.1		5.2	

Neutralization:

(3) $NH_4HSO_3 + NH_4OH \rightarrow (NH_4)_2SO_3 + H_2O$

In the neutralizer, ammonium bisulfite is converted to ammonium sulfite

Oxidation:

(4) $2(NH_4)_2SO_3 + O_2 \rightarrow 2(NH_4)_2SO_4$

In the oxidizer, the oxidation of ammonium sulfite yields a solution of ammonium sulfate as byproduct of the process.

A common parameter in the ammonia-based process is S/C_A ratio,[159,160] in which S is defined as moles of SO_2 (as ammonium sulfite and bisulfite) per 100 moles of water, and C_A is defined as moles of NH_3 (as ammonium sulfite and bisulfite) per 100 moles of water.

The chemistry of the ammonia-based system is relatively simple. In the pH range 4.2 to 7.0 the main dissolved species are HSO_3^-, $SO_3^=$, and NH^+. The formation of sulfate depends on the amount of SO_3 in the flue gas and the degree of absorber oxidation. Other materials introduced with the gas (ash, chlorides, etc.) may accumulate if the absorber circuit is a closed loop. These materials do not appear to affect absorber efficiency.[160]

The S/C_A ratio is related to the pH of the scrubbing liquor in the absorber. The C_A value could vary from 10 to 20, with a typical C_A range of 10 to 14.[159-161] Curves of SO_2 partial pressures over $(NH_4)_2SO_4$-NH_4HSO_3-H_2O solutions versus S at constant C_A show the difficulty of obtaining high bisulfite values (high S/C_A) unless the SO_2 partial pressure in the entering gas is relatively high. Therefore, high-sulfur coal could improve economics by increasing sulfur throughput and also could allow high bisulfite-sulfite ratios for processes that are helped by a high S/C_A.[160]

Mass transfer in SO_2 absorption by an ammoniacal solution is controlled mainly by the gas phase resistance. The chemical reactions involved are rapid; hydration of SO_2 is the slowest but it is fast enough to be nonlimiting up to a concentration of 3 to 4 percent SO_2 in the gas. Liquid film resistance is also quite low, except at low pH which would be encountered in the first stage of a multistage absorber; the liquid-phase resistance becomes equal to the gas-phase resistance at an S/C_A of 0.92 to 0.96. The transfer rate falls rapidly with increasing temperature. Thus, cooling below the wet bulb temperature, although expensive, would yield better SO_2 absorption by the absorbing solution.[160]

Assuming an S/C_A ratio of 0.79 at pH 5.8, the ammonia requirement is 1.29 moles NH_3/mole of SO_2 removed and the composition of the bleed-off solution is about 71.4 mole percent NH_4HSO_3, 26.0 mole percent $(NH_4)_2SO_3$, and 2.6 mole percent $(NH_4)_2SO_4$. After neutralization and oxidation the solution typically has 24 weight percent $(NH_4)_2SO_4$.

The chemistry involved in the regenerable process depends entirely on the nature of the product. Detailed reliable data are available.[162-165]

System description--The nonregenerable ammonia-based processes have been widely used to control SO_2 emissions from various industrial process sources such as pulp and paper plants[166] and sulfuric acid plants,[167],[168] and to a lesser degree from industrial boiler sources.[169] No commercial application of an ammonia-based FGD system in the U.S. utility industry has been reported. The high energy requirement and unfavorable economics[170] of a regenerable, ammonia-based process have prohibited its use in that application.

The three major operations[171],[172] of a nonregenerable ammonia-based FGD system are as follows:

- Flue gas pretreatment--particulate removal as required, and cooling and humidification in a quencher.
- SO_2 absorption--removal of SO_2 by reaction with ammoniacal liquor in the absorber.
- Neutralization and oxidation--the bleed-off solution is neutralized by pure ammonia in a neutralizer and later oxidized by air.

Figure 4.2-25 presents a typical process flow diagram for such a system. Flue gas from a stationary source, depending on its particulate concentration, may pass through a particulate collection device before entering a quencher (Q-1). Flue gas with low particulate content enters the quencher through a forced draft (FD) fan (F-1). In the quencher the flue gas is cooled to its adiabatic saturation temperature by recirculating

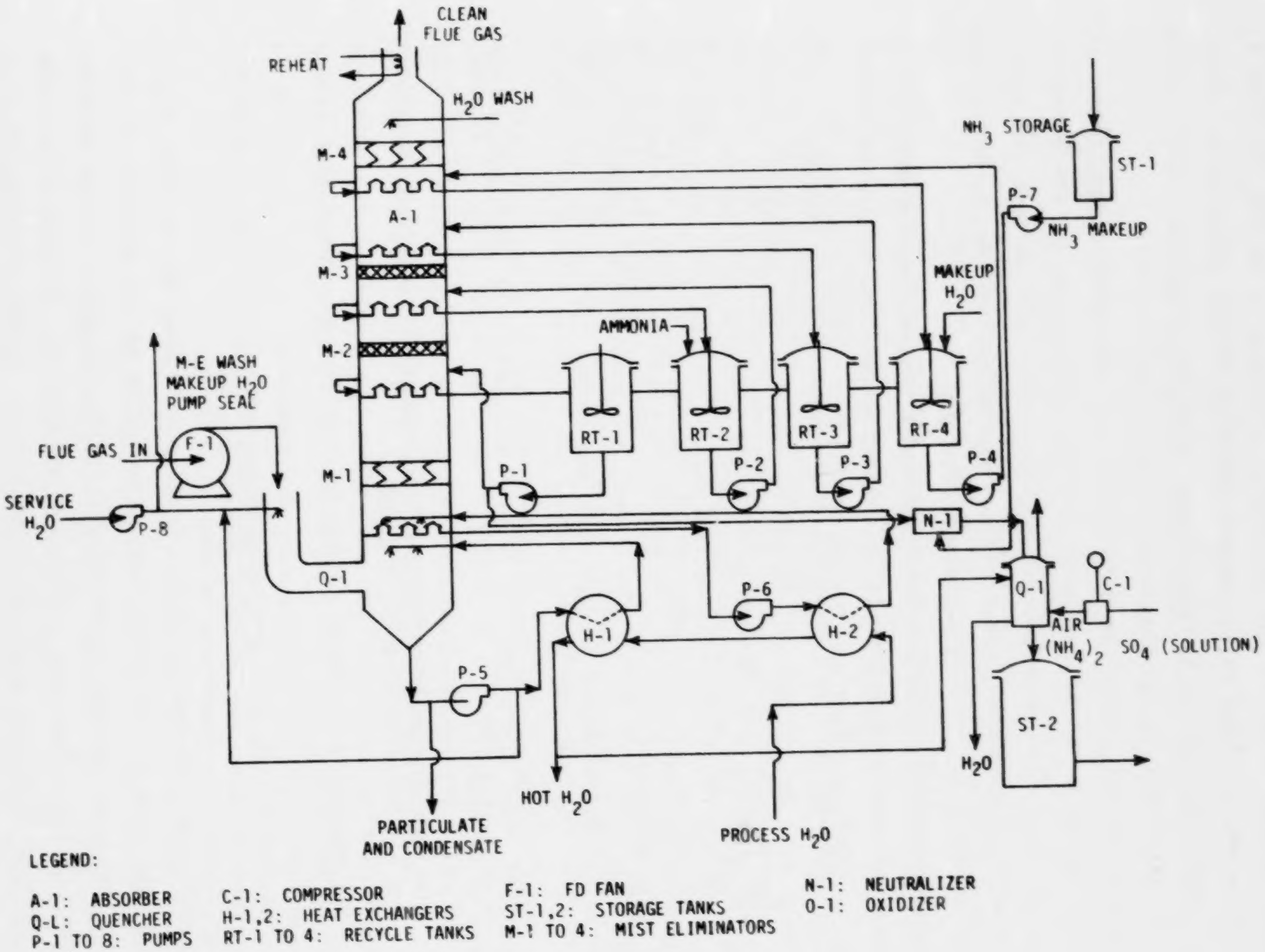

CLEAN FLUE GAS
REHEAT
H$_2$O WASH
M-4
A-1
M-3
M-2
M-1
Q-1
M-E WASH
MAKEUP H$_2$O
PUMP SEAL
FLUE GAS IN
F-1
SERVICE H$_2$O
P-8
P-1
P-5
AMMONIA
RT-1
RT-2
RT-3
RT-4
P-2
P-3
P-4
MAKEUP H$_2$O
NH$_3$ STORAGE
ST-1
P-7
NH$_3$ MAKEUP
N-1
P-6
H-1
H-2
Q-1
C-1
AIR
(NH$_4$)$_2$ SO$_4$ (SOLUTION)
ST-2
H$_2$O
HOT H$_2$O
PARTICULATE AND CONDENSATE
PROCESS H$_2$O
LEGEND:
A-1: ABSORBER
Q-L: QUENCHER
P-1 TO 8: PUMPS
C-1: COMPRESSOR
H-1,2: HEAT EXCHANGERS
RT-1 TO 4: RECYCLE TANKS
F-1: FD FAN
ST-1,2: STORAGE TANKS
M-1 TO 4: MIST ELIMINATORS
N-1: NEUTRALIZER
O-1: OXIDIZER

Figure 4.2-25. Nonregenerable ammonia-based process.

water. As a means of controlling the formation of ammonia fumes (sometimes called "blue haze") in the exit gas (a problem in most of the earlier ammonia absorber applications),[173] the gas must be cooled to temperatures below its adiabatic saturation temperature. This is accomplished in two cooling stages that precede the absorption section. Heat exchangers are supplied for each stage to cool the recirculating water.

The cooled flue gas enters the absorber (A-1), which incorporates four stages. The first three stages are required to maximize SO_2 absorption and to minimize ammonia loss and fume formation. The final stage is mainly a water wash, which removes entrained absorber liquor. The four absorption stages have valve trays, which are independent of each other. Absorber efficiency is increased by placing mobile plastic spheres on the first two absorption stages. A pad-type (wire mesh) mist eliminator follows each stage. Chevron-type mist eliminators are installed above the cooling and absorption stages.

Makeup water is added to the fourth-stage recycle tank (RT-4). Recycle tanks are arranged in such a way that liquor can flow successively from the fourth stage to the lower stages. The proper concentration at each stage can be maintained by monitoring the flow rates of bleed-off between stages and the product bleed-off.

The product bleed-off liquor from the first stage passes through a neutralizer (N-1), where the liquor is neutralized to ammonium sulfite. Ammonia is fed to the neutralizer and the second absorption stage from a storage tank (ST-1). The neutralized liquor is then oxidized to ammonium sulfate by compressed air in the oxidizer (O-1). The 24 weight percent solution of ammonium sulfate is stored in a tank (ST-2).

The water used in the heat exchangers represents a substantial recovery of heat, which may be utilized within the plant for preheating the boiler feed water or other process uses.[171]

Formation of ammonia fume is minimized by reheating of the clean flue gas, which then leaves the system through a stack.

The ammonium sulfate generated in the process is a widely used fertilizer, second only to ammonium nitrate as a world source of fertilizer nitrogen.[174] Oxidation of neutralized liquor is an old and fairly well-established practice, considered as the basic method of converting the entire bleed-off liquor to sulfate. The dilute solution of ammonium sulfate can be directly sold or concentrated and crystallized. Although oxidation is a relatively simple method of sulfite conversion, use of the byproduct is sometimes a problem. Industries such as caprolactam and coke manufacturing produce large quantities of byproduct ammonium sulfate.[174],[175]

Absorber design and types--The ammonia-based process differs from other systems using alkalis in that both the cation and the anion are volatile; therefore the absorber must be designed to recover both. In processes that require a high bisulfite content in the absorber effluent liquor, an enriching stage is needed in which the driving force of the SO_2 partial pressure in the incoming gas produces a high bisulfite-sulfite ratio. In practice, four or more stages are preferable for maximizing the bisulfite content. The composition of the solution circulated in each stage is controlled.[160]

Several different absorber types have been used in ammonia-based processes: a venturi/separator combination in an industrial boiler particulate and SO_2 removal system;[169] bubble cap and tray tower absorbers in pulp and paper plants;[176] a two-stage, packed-bed tower with Brink mist eliminators in sulfuric acid plants;[167] and sieve tray impinger-type absorbers in other miscellaneous plants.[168] Comparison of the performance data is difficult because of widely varying conditions. In an effort to obtain comparative data, the EPA and the Tennessee Valley Authority (TVA) installed a pilot plant at TVA's Colbert station in Tuscumbia, Alabama.[160] Various absorbers have been tested, including tray, plate, and mobile-bed types. Each absorber has given good SO_2 removal, but some offer advantageous operational features. A valve tray arrangement, widely used in pulp and paper mills for SO_2 control, is a variation of the bubble-cap arrangement.[172],[176] The valve trays are, in effect, perforated trays with variable openings for gas flow. The perforations are covered with movable caps, which rise as the rate of gas flow increases. At low gas flows, with correspondingly small openings, the tendency to weep is reduced; at high gas flows the pressure drop remains low. Many varieties of valve tray absorbers are available.

Nonregenerable processes[177]--For some years now, the ammonia process has been used to remove SO_2 from flue gases emanating at pulp mills. In particular, one pulp mill with scrubbers ranging from 5.2 to 7.6 m (17 to 25 ft) in diameter and from 18 to 27 m (60 to 90 ft) high successfully removed both particulate and SO_2 from recovery boiler flue gases. The scrubbers serving these installations are handling gases equivalent to coal-fired boilers ranging from 80- to 100-MW capacity.[177]

Regenerable processes--The research effort on ammonia as an absorbent for SO_2 has included studies of a wide variety of regenerable processes.[178] One way of regenerating the absorber solution is by thermal stripping. In this process the bleed-off solution is heated to evolve SO_2. The process apparently is not considered economical.[178]

Catalytic, Inc., and Institut Francais du Petrole (IFP) have developed a regenerable process with elemental sulfur as the end product. The process uses a staged absorber, a sulfate reducer, and a liquid Claus reactor. A low-Btu gas produced from coal and rich in hydrogen and carbon monoxide is utilized to reduce ammonium sulfate and sulfur trioxide, to produce hydrogen sulfide for the Claus reaction, and to incinerate the tail gas. Major problems associated with this process are the possible formation of a 'blue plume' and lack of commercial scale equipment for the sulfate reducer and H_2S generator.[164]

Another regenerable process is the ammonia-ammonium bisulfate (ABS) process developed by TVA, which removes SO_2 from the flue gas by absorption in a buffered aqueous solution of ammonium sulfite and bisulfite. The solution is regenerated by acidulation to release the SO_2, and produce ammonium sulfate solution. In an integrated ABS process, acidulation occurs when ammonium bisulfate is generated by thermal decomposition of ammonium sulfate. The liquor from the acidulator overflows into a stripper where the remaining SO_2 is stripped with air. The stripped liquor is sent to an evaporator-crystallizer to produce a slurry of ammonium sulfate crystals. The crystals are fed to the ammonium sulfate decomposer.

Ammonia fumes in the exit gas--One of the most difficult problems in the ammonia-based process is fume formation. The most complete evaluations of fume formation have been done concurrently by Air Products, Inc./ Catalytic, Inc., and by TVA/EPA. The approaches are different, one being theoretical and the other based primarily on pilot plant operation. Regardless of the basis, these studies show that control of the partial pressures of gaseous ammonia, SO_2, and water vapor in each absorption stage is critical to prevention of ammonia fumes.[173] The average particle size in the fume has been determined to be about 0.25 μm, with 10^7 particles per cubic centimeter in the size range of 0.005 to 0.5 mm. Chemical and petrographic analyses of the plume collected in an impaction sampler indicate that the major fraction of the ammonia-sulfur salt is ammonium sulfate. The particulates probably were formed in the vapor phase as ammonium sulfite and then oxidized to the sulfate form in the sampler. A portion of the particulate was analyzed as ammonium chloride.[179]

The TVA pilot tests showed that a water wash ahead of the absorber materially reduced the chloride content of the entering gas. This also would reduce plume formation.[179]

Another means of fume control is to allow the fume to form and simply remove it in a candle-type mist eliminator. Some sulfuric acid plants use such mist eliminators in the absorbers to control fumes in the exit gas.[167] Certain candle-type mist eliminators can eliminate liquid mist of sizes as low as 0.1 μm with over 99 percent efficiency.[180]

Costs--Various estimates of capital and operating costs of ammonia-based processes differ for regenerable and nonregenerable processes, depending on the specific installation.[181-183] The operating cost of an FGD facility is significantly affected by the SO_2 content in the flue gas treated and the prices of both ammonia and the byproducts.

Table 4.2-21 summarizes the estimates of capital and operating costs for an ammonia-based process that controls SO_2 emissions from a coal-fired boiler and yields byproduct ammonium sulfate. The total installed cost includes all material, labor, engineering, procurement services, supervision for design and erection of the facility, contingencies, and contractor's fees. These costs, however, do not include land or allowance for site preparation.

Detailed cost estimates were made for a regenerable, ammonia-based process with byproduct sulfuric acid and a nonregenerable ammonia-based process with byproduct ammonium sulfate.[182] Table 4.2-22 summarizes the

TABLE 4.2-21. SUMMARY OF ESTIMATED CAPITAL AND OPERATING COSTS FOR A NONREGENERABLE, AMMONIA-BASED PROCESS WITH AMMONIUM SULFATE PRODUCTION[a]
(millions of mid-1979 dollars)

	Plant size		
	100 MW	50 MW	25 MW
Capital Cost			
Fixed capital investment	12.3	8.1	6.2
Working capital	1.8	1.2	0.9
Total capital investment	14.1	9.3	7.1
Operating Cost			
Raw material cost-NH_3 at $115/ton	1.60	0.80	0.40
Conversion costs[b]	2.00	1.40	1.10
Total direct cost	3.60	2.20	1.50
Total Indirect Cost[c]	2.50	1.80	1.40
Total Direct and Indirect Cost	6.10	4.00	2.90
Byproduct credit at $55/ton	(2.54)	(1.20)	(0.60)
General and administrative expenses	0.73	0.54	0.45
Total Annual Revenue Requirements	4.29	3.34	2.75

[a] Basis: coal 3.5 percent sulfur content, 90 percent SO_2 removal, 90 percent capacity factor, remaining plant life of 10 yr, U.S. Gulf Coast plant location.

[b] Includes cost of utilities, labor and supervision, maintenance and repairs, supplies, and laboratory operations.

[c] Includes cost of payroll, overhead, depreciation, taxes, and insurance.

TABLE 4.2-22. SUMMARY OF ESTIMATED CAPITAL AND OPERATING COSTS FOR AN AMMONIA-BASED FGD FACILITY ON A NEW 500-MW COAL-FIRED POWER UNIT[a] (millions of mid-1979 dollars)

	Process type	
	Regenerable, sulfuric acid production	Nonregenerable, ammonium sulfate production
Capital Cost		
Direct capital investment[b]	33.8	25.3
Engineering design, field expense, contractor fees, and contingency	12.5	9.4
Fixed capital investment	46.3	34.7
Land, working capital, and interest during construction	10.2	8.1
Total Capital Investment	56.5	42.8
Operating Cost		
Cost of raw material[c]	1.22	7.50
Conversion costs[d]	7.35	5.60
Total direct costs	8.57	13.10
Total Indirect Costs[e]	10.58	8.30
Total Direct and Indirect Costs	19.15	21.40
Byproduct sales revenue[f]	(4.86)	(8.40)
Total Annual Revenue Requirements	14.29	13.00

[a] Basis: 3.5 percent sulfur in coal; 90 percent removal; power unit on-stream time, 7000 h/yr; stack gas reheat to 80°C (175°F) by indirect steam reheat; entrained water 0.5 percent by weight (wet basis); Midwest plant location; remaining life of power plant, 30 yr.

[b] Includes cost of equipment and facilities for makeup handling and preparation; particulate removal; SO_2 absorption; reheat; flue gas handling; byproduct manufacture, handling, and storage; utilities; and construction services.

[c] Includes cost of catalyst for regenerable process; NH_3 at $150/ton.

[d] Includes cost of operating labor and supervision, utilities, maintenance, and supplies.

[e] Includes cost of payroll overhead, depreciation, taxes, and insurance.

[f] Byproduct sale at $39/ton for 100 percent sulfuric acid and $57/ton for ammonium sulfate.

estimates of capital and operating costs for an FGD system on a new 500-MW coal-fired power unit firing 3.5 percent sulfur fuel. Table 4.2-23 summarizes cost estimates for ammonia-based processes and for several other advanced FGD processes.[184]

Note that annual revenue requirement is reduced significantly by credit for sale of the byproducts. Requirements for particulate collection ahead of the absorber would increase the capital investment.

Energy and environmental impacts--The energy requirements of a nonregenerable ammonia-based process are less than those of many other FGD processes. The major components consuming energy are the FD fan required to overcome the pressure drop in the absorber and, to a lesser extent, process pumps. Thermal energy is also needed to reheat the gas leaving the absorber before discharge to the atmosphere. The FD fan typically requires 60 to 70 percent of the total electrical energy consumed. The total energy consumption of such a system operating on an industrial boiler is 1.0 to 1.5 percent of the total heat input to the boiler. In a typical regenerable process, the energy consumption could be as high as 3 to 5 percent of the total heat input to the boiler. The energy requirements of different process steps in a typical regenerable process with byproduct elemental sulfur are 50 to 60 percent for ammonia scrubbing, 30 to 35 percent for Claus gas preparation, and 10 to 15 percent for Claus reaction and ammonia stripping.[164]

The cooling required to condition the gas for absorption of SO_2 yields substantial heat recovery, which is normally lost in the flue gas or in any hot quench and hot scrubbing system. The recovered heat may be utilized within the plant for preheating boiler feed water or for other process use in other plants.

Although the primary environmental consideration in a flue gas desulfurization process is SO_2 removal efficiency, attention should be directed to the overall environmental effects. Most of the particulate matter in flue gas is generally removed before the gas enters the absorber. Pulp and paper plants using nonregenerable ammonia-based FGD systems are reported to have achieved SO_2 removal efficiencies as high as 95 percent with inlet gases containing 5000 to 6000 ppm SO_2.[166] Almost all particulate matter

TABLE 4.2-23. SUMMARY OF ESTIMATED CAPITAL COST OF FLUE GAS DESULFURIZATION PROCESSES[184]
(mid-1979 dollars)

	Total capital investment, million $	Net unit revenue requirement, mills/kWh
Ammonia absorption--ammonium bisulfate regeneration--sulfuric acid production[a]	54.6	4.43
Ammonia absorption--scrubbing liquors saturated with ammonium sulfate--ammonium sulfate production	40.8	3.72
Limestone slurry absorption--ponding of sludge	39.8	3.85
Magnesia slurry absorption--sulfuric acid production[b]	41.9	3.22
Sodium sulfite absorption--sulfuric acid production[b]	48.1	4.14

[a] Regeneration process.

[b] Basis: New 500-MW coal-fired power unit, 90 percent SO_2 removal. Coal 3.5 percent S (dry basis). Stack gas reheat to 80°C (175°F) by indirect steam reheat, entrained water 0.5 percent by weight (wet basis). Power unit on-stream time, 7000 h/yr. Midwest plant location, Mid-1979 costs. Investment and revenue requirements for disposal of fly ash excluded. Remaining life of power plant, 30 yr.

larger than 7 micrometers is removed in the cooling stages; some of the particulates smaller than one micrometer are also removed.[172] Chloride removal occurs during flue gas cooling.

Pilot tests of regenerable ammonia-based processes have demonstrated SO_2 removal efficiencies of more than 90 percent.[164,185] One such process is designed to remove up to 99 percent of the SO_2 with an 8 to 10 percent increase in the cost of raw materials and utilities. Designers of another regenerable process claim to remove SO_2 and NO_x simultaneously in presence of a catalyst.[185]

Accumulation of fly ash and other particulates in the absorber bottom can be controlled or eliminated by a quencher loop purge stream.

The formation of ammonium salt fumes is an environmental consideration unique to the ammonia-based process.

Operational status and development--Ground-breaking studies in ammonia absorption date back to at least 1883, when a British patent was issued to Ramsey.[185] Exhaustive work later conducted by Johnstone and coworkers at the University of Illinois produced a collection of fundamental data that is the technical standard for current investigations.[185]

A pioneer ammonia-based SO_2 absorber began commercial service in 1936 at Consolidated Mining and Smelting Company. Ammonia absorbers are successfully applied in sulfite paper processes, where unusually severe operating requirements necessitate extremely reliable and versatile performance. With the sole exception of the 'blue plume,' ammonia absorption has been found totally acceptable. With a view toward adapting ammonia desulfurization to power plant flue gas, TVA conducted an extensive pilot program at its Colbert station.[186]

At present, ammonia-based FGD processes offered by many vendors are widely used in the pulp and paper industry, sulfuric acid plants, and other miscellaneous plants.[166-168,172] All such commercial processes are of the nonregenerable type.

Results of 3 years of operation and tests at a paper mill show that a 5000 ppm SO_2 concentration in the recovery boiler flue gases can normally be reduced below the required level of 300 ppm SO_2 in the stack effluent. At the same time, ammonia concentrations in the effluent gas are relatively low. Analyses of particulates (smaller than one micrometer) leaving the system indicate that about 20 percent is in the form of ammonium salts, most being sodium and potassium salts originating in the furnace.[172]

Seven ammonia scrubbing systems have been operating on industrial boilers, the first since October 1973 with no major problems. Great Western Sugar retrofitted ammonia-based FGD systems on lignite-firing boilers (0.7 to 1.2 percent sulfur coal). The plants operate about 3 months per year in the fall to process sugar beets. The FGD systems reportedly operate well.[187]

Several ammonia scrubbing units operating since 1977 have easily reduced the SO_2 content of sulfuric acid plant tail gas to the level required to meet emission standards.[167] These units have demonstrated the operability and reliability of the ammonia scrubbing system, though large-scale application of the system, as in the utility industry, is yet to be shown.

4.2.3.6 The Wellman-Lord Process--

In this process an aqueous sulfite solution is used to absorb SO_2. Sodium bisulfite is formed as the SO_2 is absorbed from the gas stream; the SO_2 is then released in a concentrated stream in the stripping step. The regenerated absorbent is returned to the absorber loop. The concentrated SO_2 stream with water vapor enters a condenser, where most of the water is removed. If necessary, the resulting SO_2 stream may be further dried in a concentrated sulfuric acid drying tower. Sulfur values from the SO_2 stream may be recovered as liquid SO_2, liquid SO_3, sulfuric acid, or elemental sulfur. The product is determined by potential use, market demand, and cost of transportation to the destination.

A typical Wellman-Lord system as applied to a combustion process is shown in Figure 4.2-26.

Process chemistry--In sodium sulfite/bisulfite systems, it is desirable that any fly ash or other particulate matter be removed before the absorption step to reduce the need for process purge and thereby reduce the need

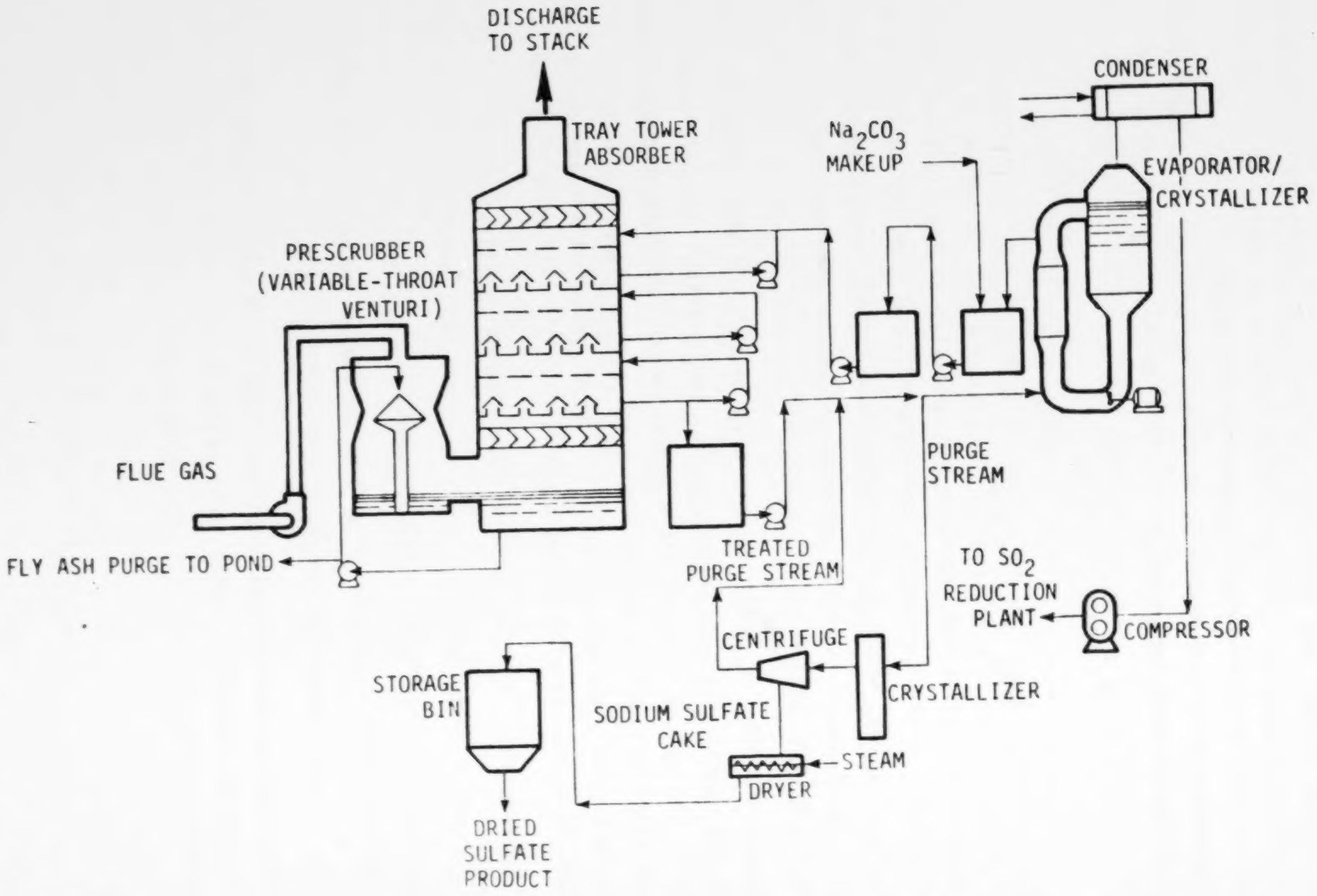

DISCHARGE TO STACK
TRAY TOWER ABSORBER
PRESCRUBBER (VARIABLE-THROAT VENTURI)
FLUE GAS
FLY ASH PURGE TO POND
Na_2CO_3 MAKEUP
CONDENSER
EVAPORATOR/ CRYSTALLIZER
PURGE STREAM
TREATED PURGE STREAM
TO SO_2 REDUCTION PLANT
COMPRESSOR
CENTRIFUGE
CRYSTALLIZER
SODIUM SULFATE CAKE
STEAM
DRYER
STORAGE BIN
DRIED SULFATE PRODUCT

Figure 4.2-26. Typical Wellman-Lord SO_2 control system.[185]

for makeup of fresh scrubbing solution. An electrostatic precipitator (ESP), fabric filter, wet particulate scrubber, or other device may be used for particulate removal. The gas stream normally is cooled to its adiabatic saturation temperature in a wet scrubber or presaturator.

The basic process for absorption of SO_2 by aqueous scrubbing liquor is given by the following reactions:

(1) $SO_{2\,(g)} \rightarrow SO_{2\,(aq)}$

(2) $SO_{2\,(aq)} + H_2O \rightarrow H_2SO_3 \rightarrow HSO_3{-} + H^+$

(3) $HSO_3 \rightarrow H^+ + SO_3^=$

Recovery processes are based on the chemistry of the sulfite/bisulfite buffer system. After appropriate pretreatment, the flue gas containing SO_2 enters the absorber, where it is brought into contact countercurrently with a sulfite solution. The sulfite absorbs and reacts chemically with the SO_2, forming the more soluble bisulfite product.[189]

Oxygen and SO_3 in the flue gas also react with the sodium sulfite, forming the unreactive sulfate/bisulfite. The presence of the unreactive species in the system necessitates a purge from the absorber to maintain the level of reactive sulfite and to reduce the possibility of scaling.[190],[191]

The principal chemical reactions in the SO_2 absorber are absorption and oxidation, discussed briefly as follows:[192]

SO_2 Absorption: Sulfur dioxide and sodium sulfite react to form bisulfite.

(4) $SO_2 + SO_3^= + H_2O \rightarrow 2HSO_3^-$

Oxidation: Some oxidation of sodium sulfite to sodium sulfate occurs.

(5) $2SO_3 + O_2 \rightarrow 2SO_4^=$

In the sodium ion makeup reactions, sodium carbonate (soda ash) or sodium hydroxide (caustic) reacts with sodium bisulfite to regenerate the SO_2 absorbent, sodium sulfite.

(6) $Na_2CO_3 + 2NaHSO_3 \rightarrow 2Na_2SO_3 + H_2O + CO_2\uparrow$

(7) $NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O$

If the product is to be a concentrated SO_2 stream, the bleed stream is regenerated by use of single-effect evaporators, double-effect evaporators, or either atmospheric or vacuum steam stripping. The basic chemical reaction for regeneration of the alkali absorbent is then:

(8) $2NaHSO_3 \overset{\Delta}{\rightarrow} Na_2SO_3 + H_2O\uparrow + SO_2\uparrow$

The sodium sulfate formed by oxidation of sulfite or by absorption of SO_3 must be purged at approximately the rate of formation. It can be dried for sale or disposal, or it can be neutralized and discharged as an innocuous effluent.

The concentrated SO_2 stream leaving the regeneration step can be used to produce sulfuric acid, sulfur, liquid SO_2, or some combination of these, depending on available markets. The chemistry of these regeneration processes is as follows:

Sulfuric Acid: Sulfur dioxide reacts with oxygen in the presence of vanadium pentoxide catalyst to form SO_3.

(9) $2SO_2 + O_2 \rightarrow 2SO_3$

The SO_3 reacts with water to form sulfuric acid.

(10) $SO_3 + H_2O \rightarrow H_2SO_4$

These are the reactions that occur in a typical sulfuric acid plant.

Sulfur: Methane (natural gas) reacts with SO_2 to form hydrogen sulfide.

(11) $2CH_4 + 3SO_2 \rightarrow 2CO_2 + 2H_2O + 2H_2S + S$

The hydrogen sulfide reacts with sulfur dioxide to form water vapor and sulfur.

(12) $2H_2S + SO_2 \rightarrow 2H_2O + 3S$

The overall reaction is:

(13) $CH_4 + 2SO_2 \rightarrow CO_2 + 2H_2O + 2S$

Other commercially available reductants that can be used in place of methane (natural gas) are carbon monoxide, hydrogen, higher hydrocarbons up through propane, and the products of coal gasification (low-, medium-, and high-Btu coal gases).

Liquid SO_2: The SO_2 vapors contact silica gel to remove moisture. The vapors then are compressed and condensed; the resulting liquid is collected and stored in pressurized tanks.

Liquid SO_3: The SO_2 reacts with oxygen in the presence of vanadium pentoxide catalyst to form SO_3, which is then compressed, condensed, and stored in pressurized tanks.

System description--A sulfite/bisulfite FGD system can be considered in terms of the following general steps:

- Flue gas pretreatment
- SO_2 absorption
- Absorbent regeneration
- Sulfur product recovery
- Purge treatment

Efficient flue gas pretreatment is important to these FGD systems because, in reducing particulate contamination, the requirements for regeneration and purge are reduced. The flue gas to be treated is taken after the electrostatic precipitator at a temperature of about 149°C (300°F) and passed through a venturi or tray-type prescrubber, in which it is cooled to around 54°C (130°F) and humidified. A tray-type prescrubber satisfactorily cools and humidifies the gas with low pressure drop, but removes less of the fly ash and chlorides. Humidification of the flue gas in the prescrubber prevents the evaporation of excessive amounts of water in the absorber. Scaling and plugging problems are virtually eliminated by use of the prescrubber and clear scrubber solutions as well as by the solubility of the absorption product, sodium bisulfite, which is more soluble than sodium sulfite.

A well-designed prescrubber removes up to 99 percent of all chlorides in the flue gas; this should help maintain a low level of chloride in the scrubbing liquor and reduce the potential for stress corrosion. The absorption of chlorides and some SO_2 and SO_3 can cause the scrubber water to become acidic. After neutralization with lime when necessary, the fly ash and other solids collected by the prescrubber are pumped to an ash disposal pond as about a 5 percent slurry.

The SO_2 absorption step in the Wellman-Lord process has been performed primarily in a tray tower absorber. The humidified gas from the prescrubber is passed upward through the absorption tower, where it meets the countercurrent flow of the aqueous absorbent solution. The Wellman-Lord systems at both NIPSCO and Public Service of New Mexico have shown individual SO_2 removal test results above 90 percent.[193-195] Mist elimination can be achieved with either chevron-type or polypropylene-mesh-type units. Reheat of about 28°C (50°F) is often practiced to reduce condensation and the resulting potential for corrosion downstream from the absorber.

When SO_2 is the product of the regeneration step, various sulfur products are possible. Production of elemental sulfur, which has been done at two full-scale utility FGD systems, requires a reducing gas (such as methane or natural gas, hydrogen sulfide, or carbon monoxide).[196]

Sulfuric acid, the most widely used commodity chemical in the world, is another possible product. Although acid production consumes less energy than the production of elemental sulfur, the availability of a market in the area must be considered.[197] Since sulfuric acid is a byproduct, a definite market is needed to maintain proper operation of the FGD system. The Public Service of New Mexico, San Juan Station will produce sulfuric acid directly when Unit 4 comes on stream.[198]

Other options are to produce liquid SO_2 or SO_3; however, the market for these chemicals is relatively small. A decision to produce either would be site specific.

In addition to the decision regarding the byproduct materials, disposal of the purge stream must be considered. Some of the sodium sulfite in the absorbent solution will be oxidized to sodium sulfate. The degree of sulfate generation is a function of the SO_3 content of the incoming gas stream and the excess oxygen. Since the sulfate form has no SO_2- absorbing value, it must be purged from the process. The sodium sulfate, present in the decahydrate form (Glauber's salt), is continuously removed from the regenerated absorbent solution by vacuum crystallization. Subsequently, it is prepared for disposal or dried for storage and sale. The sodium sulfate is used in the pulp and paper industry and the fertilizer industry, two of several potential markets.

Operational status and current developments--The Wellman-Lord process, a proprietary process of Davy McKee, Inc. (formerly Davy Powergas), is in wide use both in Japan and the United States. In Japan, the Wellman-Lord process is used on 14 oil-fired boilers and 3 Claus sulfur plants; 3 of the 14 oil-fired boilers are electric generation units.[199] In the United States, the process is used on four Claus sulfur plants, two sulfuric acid plants, and three coal-fired electric generation units.[200] Units are under construction for two more coal-fired electric generation units and three coke-fired boilers.[200] Tables 4.2-24 and 4.2-25 give more details regarding these units.

The first large installation of a Wellman-Lord unit at a Japanese utility plant came on line in late spring of 1973 at the Nagoya Station of the Chubu Electric Power Company. The unit, constructed almost entirely of stainless steel, has the capacity of treating 663,000 m^3/h (390,000 scfm) of flue gas, containing 2100 ppm SO_2, from a 220-MW boiler that burns oil containing 3 percent sulfur. It was designed and constructed by Mitsubishi Kakoki Kaisha, a licensee of Davy McKee, Inc. The Nagoya station is a peak-shaving power plant. The FGD system was contractually required to handle stack gas fluctuations from 35 to 105 percent of design flow in 22 minutes, while maintaining outlet SO_2 emissions at less than 150 ppm. In May 1973 the Japanese government measured the outlet SO_2 at 130 to 135 ppm, which represents over 93 percent SO_2 removal.[201]

The flue gas from the boiler is cleaned in an ESP and precooled to 58°C (136°F) before entering the tray absorber. The L/G ratio is 0.7 liter/Nm^3 (5.2 gal/1000 scf).[202]

When the unit was originally put on line, the operators inadvertently switched from low-sulfur (0.7%) to high-sulfur (4%) fuel oil; this change had little effect on the outlet SO_2 concentration, however, and because of automated adjustments of the process equipment the concentration did not exceed 150 ppm.[203]

The Nagoya unit has proved reliable and easy to control. The system is highly automated; only two operators are needed for the entire operation,

TABLE 4.2-24. WELLMAN-LORD PLANT INSTALLATIONS IN THE UNITED STATES[200]

Company and location	Feed gas origin	Gas volume treated, Nm^3/s (scfm)	Disposition of SO_2
Units on stream			
Olin Corp./Paulsboro, N.J. (now shut down)	Sulfuric acid plant	21 (45,000)	Recycle to acid plant
Standard Oil of California/El Segundo, Calif.	Claus plant	14 (30,000)	Recycle to Claus plant
Allied Chem./Calumet, Ill.	Sulfuric acid plant	14 (30,000)	Recycle to acid plant
Olin Corp./Curtis Bay, Md.	Sulfuric Acid Plant	37 (78,000)	Recycle to acid plant
Standard Oil of California/Richmond, Calif.	Claus plant	14 (30,000)	Recycle to Claus plant
Standard Oil of California/Richmond, Calif.	Claus plant	14 (30,000)	Recycle to Claus plant
Standard Oil of California/El Segundo, Calif.	Claus plant	14 (30,000)	Recycle to Claus plant
Northern Indiana Public Service Company/ Gary, Ind.	115-MW coal-fired power plant	146 (310,000)	Elemental sulfur plant
Public Service Company of New Mexico/ Waterflow, N.M.	700-MW coal-fired power plant (2 boilers)	887 (1,880,000)	Elemental sulfur plant
Units in design or construction			
Public Service Company of New Mexico/ Waterflow, N.M.	1100-MW coal-fired power plant (2 boilers)	1,287 (2,727,000)	Sulfuric acid plant
Getty/Delaware City, Del.	Three coke-fired boilers	236 (500,000)	Sulfuric acid plant

TABLE 4.2-25. WELLMAN-LORD PLANT INSTALLATIONS OVERSEAS[199]

Company and location	Feed gas origin	Gas volume treated, Nm^3/s (scfm)	Disposition of SO_2
Japan Syn. Rubber/Chiba	Oil-fired boiler	59 (124,000)	Sulfuric acid plant
Toa Nenryo/Kawasaki	Claus plant	19 (41,000)	Recycle to Claus plant
Chubu Electric/Nagoya	220-MW oil-fired power plant	184 (390,000)	Sulfuric acid plant
Japan Syn. Rubber/Yokkaichi	Oil-fired boiler	132 (280,000)	Sulfuric acid plant
Sumitomo Chem./Sodegaura	Oil-fired boiler	106 (225,000)	Sulfuric acid plant
Kashima Oil/Kashima	Claus plant	9 (20,000)	Recycle to Claus plant
Mitsubishi Chem./Mitzushima	Oil-fired boiler	176 (373,000)	Sulfuric acid plant
Toa Nenryo/Hatsushima	Claus plant	5 (10,000)	Recycle to Claus plant
Toyo Rayon/Nagoya	Oil-fired boiler	103 (218,000)	Sulfuric acid plant
Japan Nat. Railroad/Kawasaki	200-MW oil-fired power plant	205 (435,000)	Sulfuric acid plant
Kurashiki Rayon/Okayama	Oil-fired boiler	117 (248,000)	Sulfuric acid plant
Fuji Film/Fujinomiya	Oil-fired boiler	42 (89,000)	Liquid SO_2
Shin Daikyowa/Yokkaichi	Oil-fired boiler	119 (253,000)	Sulfuric acid plant
Sumitoma Chem./Niihama	Oil-fired boiler	43 (91,000)	Liquid SO_2
Mitsubishi Chem./Mitzushima	Oil-fired boiler	184 (390,000)	Sulfuric acid plant
Mitsubishi Chem./Kurosaki	Oil-fired boiler	156 (330,000)	Sulfuric acid plant
Tohoku Electric/Niigata	100-MW oil-fired power plant	111 (236,000)	Sulfuric acid plant

including startup and shutdown. Automation is necessary because of the widely fluctuating load and the shutdown of the boiler every weekend.

The first application of a Wellman-Lord system to a coal-fired utility boiler is the 115-MW Unit No. 11 at the D.H. Mitchell Station of Northern Indiana Public Service Company (NIPSCo). Flue gas from the boiler passes through an ESP for primary particle removal (about 98.5 percent efficiency).[204] The booster blower delivers the flue gas through a variable-throat venturi prescrubber to the absorber. The flue gas is cooled and saturated in the prescrubber by water recirculated from the bottom of the prescrubber and back to the venturi sprays. Fly ash captured by the scrubbing solution is purged continuously from the system to a fly ash pond. For short periods, the scrubber can handle considerably greater than design fly ash loading. Water from Lake Michigan is used to make up water lost through the purge and evaporation processes.[205]

Absorption of the SO_2 from the prescrubbed flue gas takes place in a three-stage absorber. Each stage consists of a valve tray and a collector tray.[206] A sodium sulfite solution absorbs and chemically reacts with the SO_2 to form sodium bisulfite. A mist eliminator removes entrained liquid droplets from the gas leaving the absorber stack. The stack incorporates a direct-fired, natural gas reheat system to heat the cleaned gas to 82°C (180°F), if necessary, to enhance dispersion of the steam plume.

The product solution collected on the bottom collector tray overflows to the absorber surge tank, from which the solution is pumped through a filter to ensure that no fly ash enters the evaporator system. A small sidestream of the filtered solution is sent to the purge treatment unit to remove the sodium sulfate. The purge treatment equipment consists of four chilled-wall crystallizers; a slurry of sodium sulfate crystals forms in the crystallizers and is then removed in a centrifuge. The resulting clear solution is pumped to the evaporator for regeneration of the sodium sulfite.

The evaporation system consists of a forced-circulation vacuum evaporator. The filtered solution is recirculated in the evaporator, where low-pressure (345 kPa, 50 psig) steam is used to evaporate the water from the sodium bisulfite solution. When enough water is removed, sodium sulfite crystals form and precipitate. Sulfur dioxide is removed with the overhead vapors. The slurry formed by the sodium sulfite crystals is withdrawn continuously to a dump/dissolving tank, where condensate from the evaporator is used to dissolve the crystals in the solution that is pumped back to the top stage of the absorber.[206]

Water vapor is removed from the SO_2 in water-cooled condensers. The SO_2 is compressed by a liquid ring compressor for introduction to an SO_2-reduction facility designed and operated by Allied Chemical. The gas stream is about 85 percent SO_2; the remainder is mostly water vapor.[206] The off-gases from the reduction facility are burned in a tail gas incinerator and are returned to the absorber inlet.

Sodium lost as sulfate in the purge treatment system is replenished by addition of sodium carbonate to the absorber solution. Soda ash is brought to the plant in trucks and transferred to the storage bin by a pneumatic conveying system. It is metered to the slurry tanks by a bin activator and belt feeder. The soda ash slurry is pumped to the absorber feed tank by parallel centrifugal pumps.

The operating history of the unit at Mitchell Station reflects both operational problems with the boiler and normal operating difficulties. The system went on line in integrated operation in November 1976. A boiler mishap in early January 1977 required a 6-month outage for boiler repair. During the demonstration period from late August to mid-September 1977, the unit met all process guarantees, including 91 percent SO_2 removal.[207] (A detailed description of actual operating performance is given in Reference 195.) Since August 1978, the operating history of the unit has been good.[208]

The largest Wellman-Lord installations are being constructed on four coal-fired boilers at the San Juan station of Public Service Company of New Mexico (PNM) in Waterflow, New Mexico. The retrofit installations on Units 1 and 2 began operation in April and September 1978, respectively.[209] An installation on the new Unit 3 boiler was completed in December 1979.[209] Unit 4 and its FGD system are scheduled for startup in January 1982.[209] Table 4.2-26 provides further details on these units.

The Wellman-Lord system for Units 1 and 2 was designed to remove 90 percent of the SO_2 from the flue gas when firing coal with sulfur content

TABLE 4.2-26. DESIGN PARAMETERS FOR WELLMAN-LORD FGD INSTALLATIONS AT SAN JUAN STATION OF PUBLIC SERVICE COMPANY OF NEW MEXICO[210]

	Unit 1	Unit 2	Unit 3	Unit 4
Boiler rating, MW (Gross)	350	350	550	550
Fuel rate, kg/h	181,440	181,440	303,458	303,458
(lb/h)	(400,000)	(400,000)	(669,000)	(699,000)
Gas flow, m^3/s (scfm) at 26.7°C (80°F)	416.2 (882,000)	373.7 (792,000)	603.7 (1,279,400)	603.7 (1,279,400)
Inlet SO_2 concentration, ppm				
Minimum	490	490	490	490
Maximum	1,200	1,200	1,200	1,200
Average	850	850	850	850
Inlet particulate loading,				
$kg/10^8$ J	0.0030	0.0043	0.0039	0.0039
$(lb/10^6$ Btu)	(0.07)	(0.10)	(0.09)	(0.09)
g/m^3	0.121	0.18	0.13	0.13
(gr/scf dry)	(0.053)	(0.079)	(0.056)	(0.056)
No. of scrubber trains[a]	4	4	5	5
m^3/s	207.2	200.1	240.8	240.8
(acfm/train)	(439,000)	(424,000)	(510,000)	(510,000)
Heating rate, kJ/kWh (Btu/kWh)				
Without scrubber	10,223 (9,682)	10,203 (9,663)	10,233 (9,691)	10,233 (9,691)
With scrubber	10,680 (10,115)	10,660 (10,096)	11,215 (10,621)	11,215 (10,621)
Sulfur produced, kg/h (ton/h) Design	2041 (2.25)	2041 (2.25)	2041 (2.25)	2041 (2.25)

[a] Each boiler will have an additional spare train to provide reserve capacity and improve reliability.

ranging from 0.59 to 1.3 percent by weight with an average of 0.8 percent. Prescrubbers with relatively high pressure drop were specified for the system because of New Mexico's stringent regulation on fine particulate emission and to provide backup for the ESP's. The purge from the prescrubber is sent to the plant wastewater system, where it is treated and then recycled.[211]

Scrubber-absorber operation does not affect the power plant operation because the FGD system can be bypassed. During a normal unit startup, scrubbers and absorbers are put on line after the ESP's are functioning.

At PNM's request, four scrubber-absorber modules were installed on each power plant unit, each sized to handle one-third of the total gas flow. Therefore, the plant has one complete spare scrubber-absorber module and can establish a maintenance program whereby absorbers are rotated in and out of service for routine and preventive maintenance. Each absorber is a five-stage tray absorber.[212]

Each scrubber-absorber module is operated independently (except for control data transmission to the control panel board), and is put on line separately. Each unit has a reheat system to protect the stack from corrosive products resulting from condensation in the flue gas when three modules are in operation simultaneously.[213]

Two 2,840,000-liter (750,000-gallon) tanks for absorber product and feed solution provide surge in the system to prevent the chemical plant operation from being affected by normal fluctuations in the scrubber-absorber area. The ideal operating situation is to have the feed solution tank full and the product tank level very low.

The chemical plant has two double-effect evaporators, which provide steam conservation (the overhead vapors from the first effect are utilized as the heat source in the second effect). For reliability, each evaporator is connected to steam and off-gas compressor manifolds so that any one evaporator can be taken out of service for maintenance without affecting the operation of the three absorber units. The availability of the chemical plant to operate depends on operation of the power generation unit. To date, this has been the major operating problem with the FGD system.[214]

The purge treatment plant consists of three low-temperature crystallizers where sodium sulfate is precipitated in the decahydrate form. The crystallizers are followed by a melt tank and evaporator. The evaporator is similar to, but smaller than, the main evaporators. Water is driven off, and the sulfate purge is centrifuged, then dried in a flash dryer. The entire purge treatment plant was specified to obtain a concentration of 70 percent sodium sulfate and 30 percent sodium sulfite in the dried purge salt. The actual sulfate content has been very high; purities have been achieved in the area of 90 percent sodium sulfate. Residual moisture in the dried purge salt has been less than 1.0 percent.[212]

Two identical Allied Chemical SO_2 reduction trains were installed as part of Units 1 and 2 FGD systems. Each of the trains has a design capacity of more than 50 percent of the total FGD system capacity, based on the use of low-grade coal (1.3% sulfur) in the boilers. Public Service Company of New Mexico specified two SO_2 reduction trains with the objective of achieving an FGD system with essentially a 100 percent onstream reliability.

The system being designed for the Units 3 and 4 power plants is somewhat similar, with the following exceptions: the prescrubbers have a lower pressure drop for energy considerations. The five-stage tray absorbers also function quite well for residual particulate removal; sulfate purge quality is not degraded because the fly ash is filtered out of the solution.

In the interest of economy the absorbers are designed for four units in operation per boiler when burning low-grade coal; therefore Units 3 and 4 will not have the one-module spare as on Units 1 and 2. The coal being used at San Juan Station has rarely exceeded 0.95 percent sulfur for long periods of time, however, so the plant operability and maintenance capability should not be affected by lack of the spare module.[212]

A sulfuric acid plant, which will be installed while the FGD system for Units 3 and 4 is being constructed, will handle the regenerated SO_2 streams from all four units. The design capacity is based on low-grade coal [470 tons (426 Mg) per day of 100% sulfuric acid]. The sulfuric acid plant will significantly reduce operating costs, reduce the demand for natural gas, directly provide the product that the sulfur is used to produce without the intermediate sulfur step, and deliver readily salable material for which there is good demand.[198]

Further current operational data on FGD systems in the United States sites are available in the quarterly EPA Utility FGD Survey.

Control cost--A recent EPA publication gives estimates of the capital costs and the operating and maintenance costs of FGD systems, including the Wellman-Lord process, which achieves 90 percent SO_2 removal while firing either of two high-sulfur eastern coals.[215] These estimates are presented in Figures 4.2-27 and 4.2-28.

The quarterly EPA Utility FGD Survey contains reported and adjusted costs for utility FGD systems. The survey data for the Northern Indiana Power unit and the two Public Service of New Mexico units are given in Table 4.2-27. The capital and operating and maintenance costs are given as reported and as adjusted to July 1979 dollars by use of the Chemical Engineering (C-E) plant cost index with the assumption of a July 1979 index of 236.5. The capital costs are in the \$150/kW range.[216]

Energy and environmental impacts--This FGD process normally has only one purge stream requiring treatment, the sodium sulfate bleed. A portion of the sodium sulfite in the absorber is oxidized to the sulfate form, which is not an absorbing species.

During the Fifth Symposium on Flue Gas Desulfurization sponsored by the U.S. EPA in Las Vegas, Nevada, in March 1979, D.W. Ross, Director of Technical Services for Davy McKee, reported that the Wellman-Lord systems at both D.H. Mitchell Station of NIPSCO and the San Juan Station of PNM have experienced about 3 percent oxidation of the absorbing liquor to the sulfate form. The sulfate (Glauber's salt) is crystallized from the purge stream and is marketed. The actual sulfate content of the crystalline purge is about 90 percent with residual moisture of less than 1 percent.

The positive side of this process is that there is a usable, salable product produced (sulfur, sulfuric acid, liquid SO_2). There is no large volume of possibly environmentally hazardous sludge that must be stored or otherwise handled and disposed of. The sodium purge product (Glauber's salt) may be salable. Regenerable sodium sulfite FGD systems are among those having the least pollution resulting from SO_2 removal.

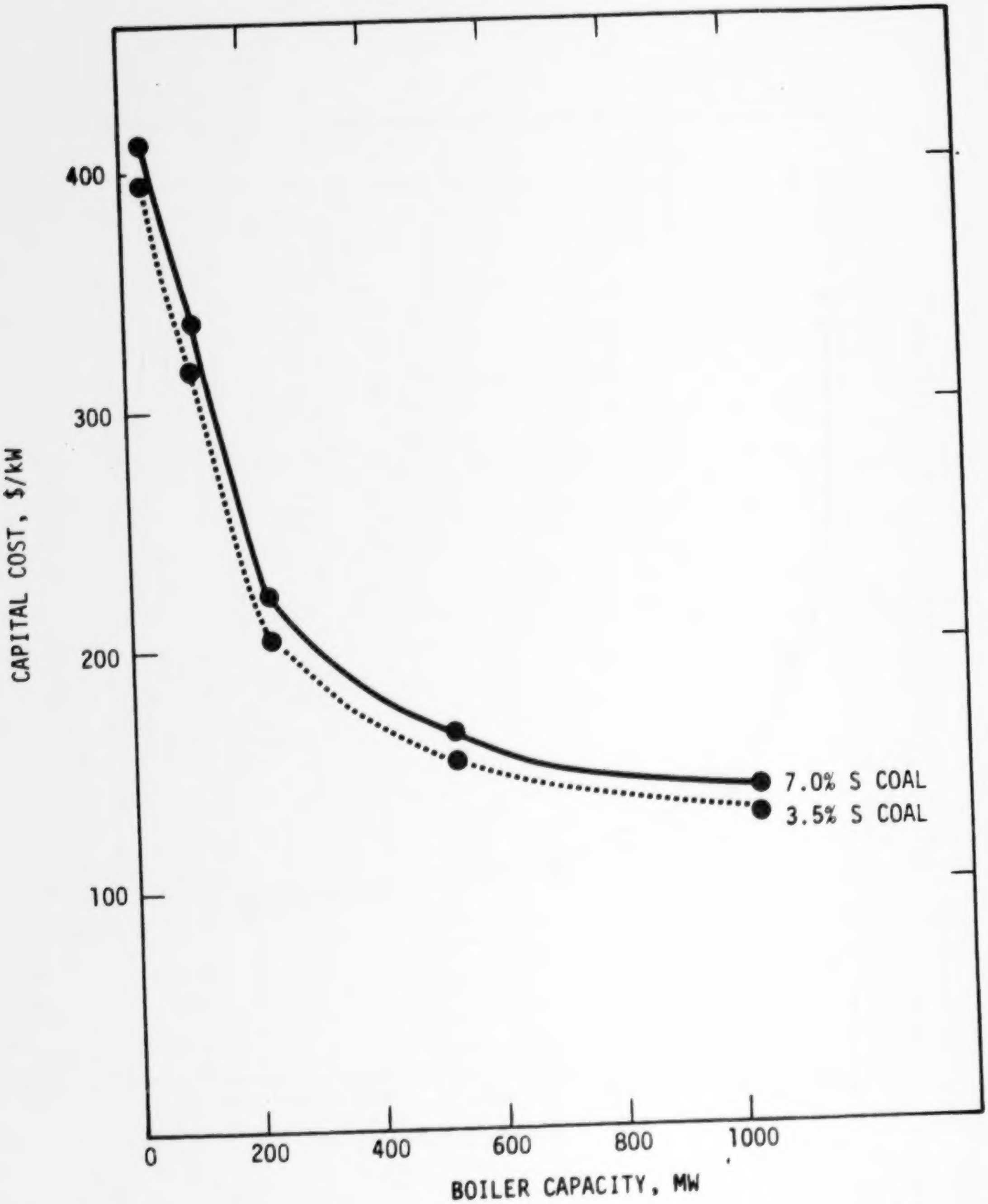


Figure 4.2-27. Estimated capital cost for Wellman-Lord FGD systems achieving 90 percent SO_2 removal firing either of two eastern coals.[215]

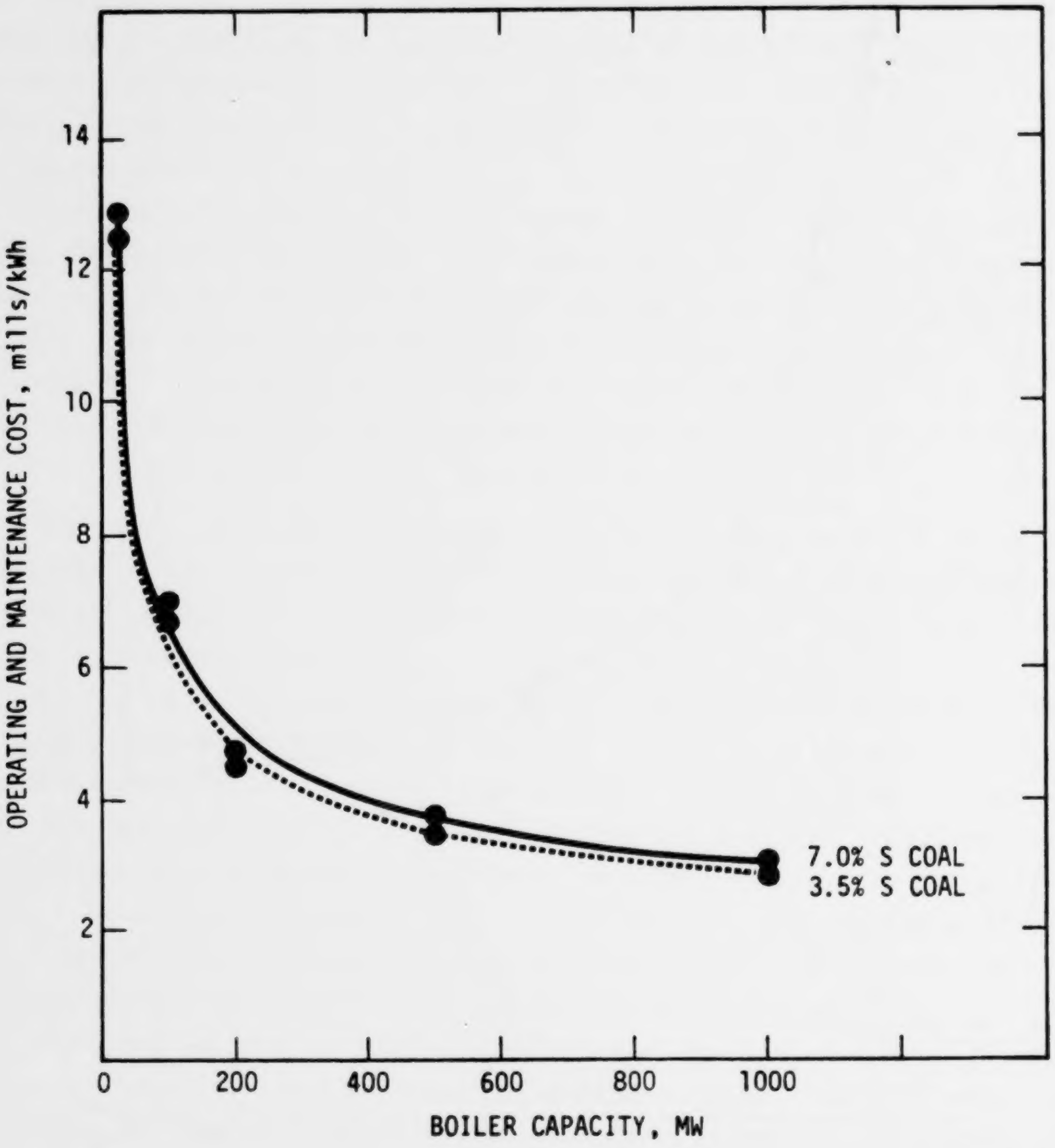


Figure 4.2-28. Estimated operating and maintenance costs for Wellman-Lord FGD systems achieving 90 percent SO_2 removal firing either of two eastern coals.[215]

TABLE 4.2-27. FGD SYSTEM ECONOMICS: OPERATIONAL SYSTEMS (REPORTED AND ADJUSTED COSTS)[216]

Utility station unit(s)	FGD MW	Elements included in capital and annual costs	Capacity factor, %	Total capital, $/kW (year)	Annual - mills/kWh		
					Total	Direct (year)	Fixed
Northern Indiana Public Service Dean H. Mitchell 11	92	a, b, c, d, e, f, g, h, i, j,	77	156.9 (1976)	Reported 14.86	6.47 (1976)	8.39
		b, c, d, e, f, h, i, j	65	168.6 (1979)	Adjusted 14.75	8.74 (1979)	6.01
Public Service of New Mexico San Juan 1	357	b, c, e, k		127.9 (1977)	Reported		
				148.2 (1979)	Adjusted		
Public Service of New Mexico San Juan 2	357	b, c, e, k		127.9 (1977)	Reported		
				148.2 (1979)	Adjusted		

[a] Particulate control (included in FGD process) included in capital cost.
[b] Total direct capital costs included.
[c] Total indirect capital costs included.
[d] Stack included in capital cost.
[e] Total regeneration facility cost included in capital cost.
[f] Total direct annual costs included.
[g] Total fixed annuay costs included.
[h] Overhead costs included in total annual costs.
[i] Particulate control costs included in direct annual costs.
[j] Replacement energy costs included in direct annual costs.
[k] Particulate control (required for FGD process) included in capital cost.

In addition to concern for the environmental impact of the FGD process, there is interest in the energy requirement of the system. In a recent EPA publication, the power consumption (energy penalty) of the Wellman-Lord FGD system is presented as a percentage of the generating capacity of the unit that it treats. The energy penalty as a percentage of gross output is shown in Table 4.2-28.[217] The energy penalty expressed in mills per kilowatt hour is shown in Table 4.2-29.[218]

4.2.3.7 The Citrate Process--

Sulfur dioxide tends to be absorbed in aqueous solutions; however, the rate of absorption is pH-dependent. The more alkaline the aqueous solution, the greater the tendency of SO_2 to be absorbed. As SO_2 is absorbed, however, the aqueous solution becomes more acidic as sulfurous acid is formed. The absorption of SO_2 in aqueous solutions, therefore, is self-limiting. By incorporating a buffering agent in the solution to inhibit the pH drop during absorption, substantially higher SO_2 loadings can be attained. This fact has led to the development of the citrate process.

Three citrate processes are or have been available: the Bureau of Mines Process, the Peabody Process, and the Flakt Process. Figure 4.2-29 shows a typical citrate process that produces elemental sulfur as the end product. Figure 4.2-30 shows a typical process that produces a concentrated SO_2 stream for possible use in sulfuric acid production or liquid SO_2 production.[219]

Process chemistry--[220-224]The primary absorbent in this process is water. The ability of the water to absorb SO_2 is enhanced by the addition of citric acid ($C_6H_8O_7 \cdot H_2O$) and either caustic (NaOH) or soda ash (Na_2CO_3).

The absorption of SO_2 occurs in three steps.

1. The solubility of SO_2 in water is limited. The SO_2 is dissolved and sets up the equilibrium:

   $$(1) \quad SO_2 + H_2O \rightleftarrows HSO_3^- + H^+$$

   The solubility of SO_2 can be increased by removing the hydrogen ions (H^+) formed. Sodium citrate (typically made by combining 0.5 m nitric acid with 1.0 m NaOH and 0.18 m $Na_2S_2O_3$) forms a stable buffer system in the 3 to 5 pH range. The buffering action of the citrate proceeds as follows where Cit is the citrate ion:

TABLE 4.2-28. ENERGY PENALTIES ASSOCIATED WITH WELLMAN-LORD SO_2 CONTROLS[217]

Coal type, % sulfur	Capacity, MW	Energy penalty, % of gross output	
		520-ng/J (1.2-lb/10^6 Btu) regulation	90% SO_2 removal
Eastern, 3.5	25	3.80	3.80
	100	3.64	3.64
	200	3.45	3.45
	500	3.34	3.34
	1000	3.25	3.25
Eastern, 7.0	25		3.80
	100		3.64
	200		3.45
	500		3.34
	1000		3.25

TABLE 4.2-29. ENERGY PENALTIES ASSOCIATED WITH WELLMAN-LORD SO_2 CONTROLS[218]

Coal type, % sulfur	Capacity, MW	Energy penalty, mills/kWh	
		520-ng/J ($1.2\text{-lb}/10^6$ Btu) regulation	90% SO_2 control
Eastern, 3.5	25	1.05	1.16
	100	1.01	1.11
	200	0.95	1.05
	500	0.92	1.02
	1000	0.90	0.99
Eastern, 7.0	25		1.16
	100		1.11
	200		1.05
	500		1.02
	1000		0.99
Western, 0.8	25		1.39
	200		1.26
	500		1.22
Anthracite	500		1.02
Lignite	500		1.02

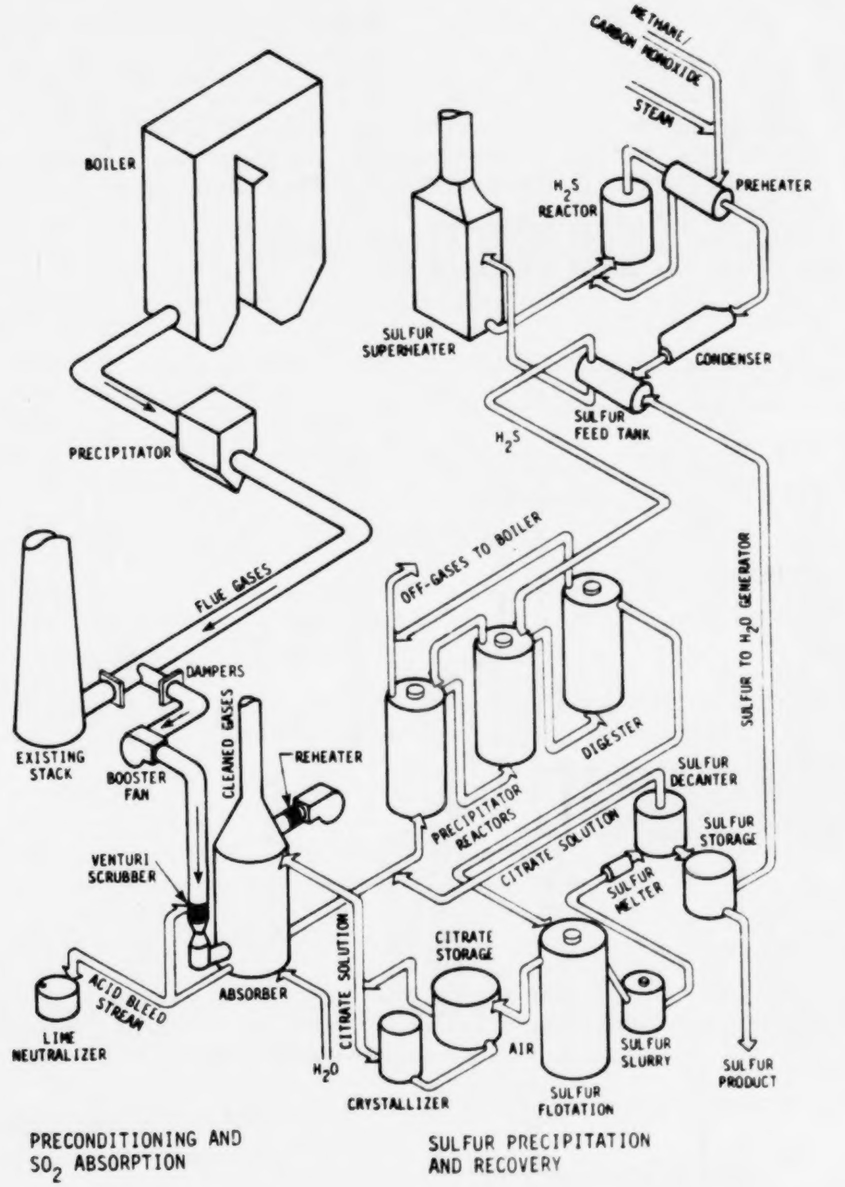

METHANE/
CARBON MONOXIDE
STEAM
BOILER
H$_2$S
REACTOR
PREHEATER
SULFUR
SUPERHEATER
CONDENSER
PRECIPITATOR
SULFUR
FEED TANK
H$_2$S
OFF-GASES TO BOILER
SULFUR TO H$_2$O GENERATOR
FLUE GASES
DAMPERS
CLEANED GASES
EXISTING
STACK
BOOSTER
FAN
REHEATER
DIGESTER
SULFUR
DECANTER
PRECIPITATOR
REACTORS
CITRATE SOLUTION
SULFUR
STORAGE
VENTURI
SCRUBBER
SULFUR
MELTER
CITRATE SOLUTION
CITRATE
STORAGE
ACID BLEED
STREAM
ABSORBER
LIME
NEUTRALIZER
H$_2$O
AIR
SULFUR
SLURRY
SULFUR
PRODUCT
CRYSTALLIZER
SULFUR
FLOTATION
PRECONDITIONING AND
SO$_2$ ABSORPTION
SULFUR PRECIPITATION
AND RECOVERY

Figure 4.2-29. Typical citrate SO_2 control process (producing sulfur product).[219]

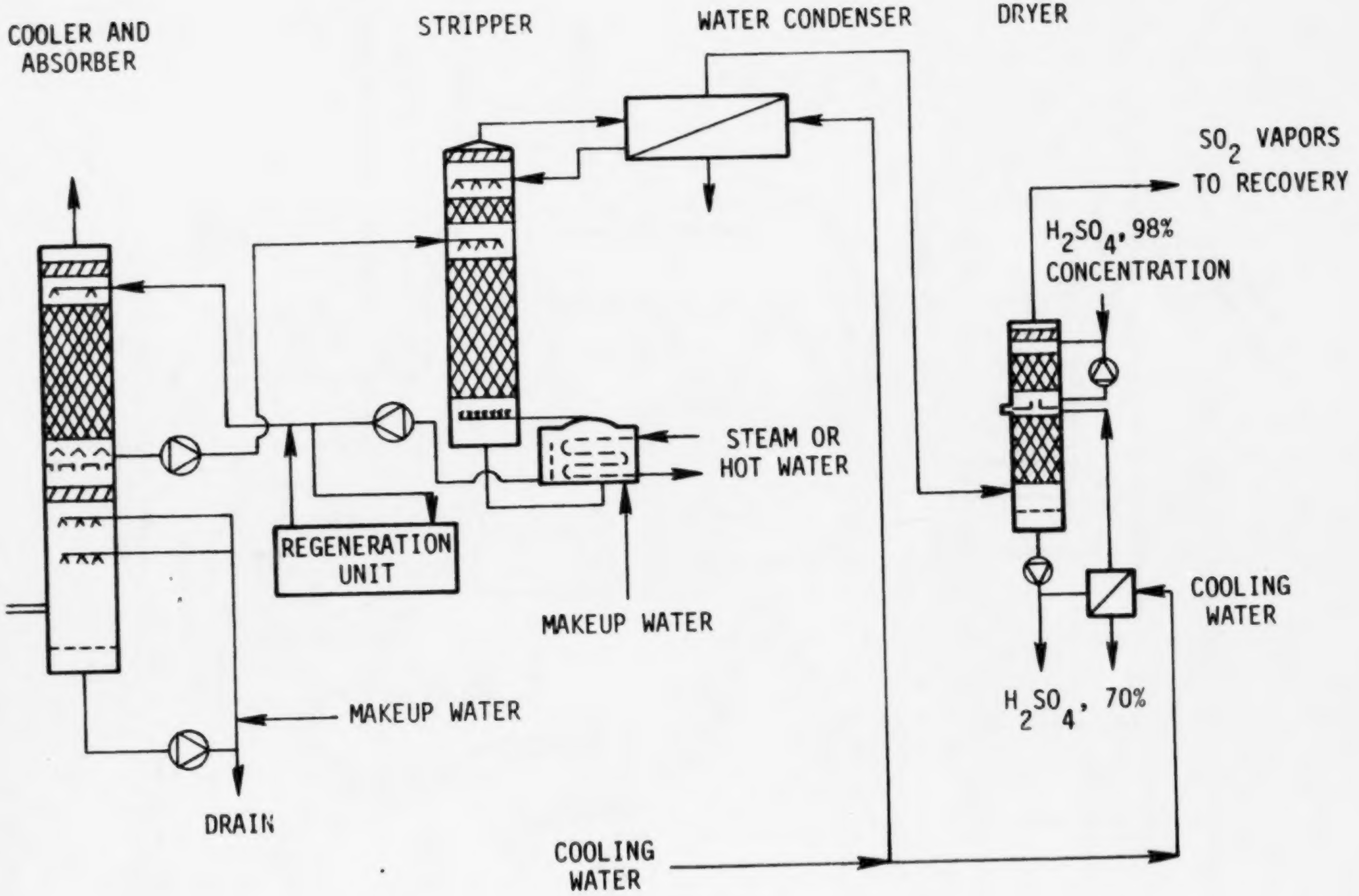

COOLER AND ABSORBER
STRIPPER
WATER CONDENSER
DRYER
SO_2 VAPORS TO RECOVERY
H_2SO_4, 98% CONCENTRATION
STEAM OR HOT WATER
REGENERATION UNIT
MAKEUP WATER
COOLING WATER
H_2SO_4, 70%
MAKEUP WATER
DRAIN
COOLING WATER

Figure 4.2-30. Typical citrate SO_2 control system (producing concentrated SO_2 vapor).

(2) $H^+ + Cit^{\equiv} \rightleftarrows HCit^=$

(3) $H^+ + HCit^= \rightleftarrows H_2Cit^-$

(4) $H^+ + H_2Cit^- \rightleftarrows H_3Cit$

Reportedly 90 percent of the SO_2 is removed in this manner.[225] Sodium hydroxide or soda ash is added to make up for sodium ions lost in the purge stream. The SO_2 absorption is a function of pH, temperature, and the SO_2 concentration of the gas stream. One source also reports the citrate/sodium ratio can play a significant role. The solubility of SO_2 increases about ten-fold for each pH unit of increased acidity. The citrate requirement of a system increases with increasing temperature and decreases with increasing SO_2 concentration in the inlet gas stream.

2. Thiosulfate ($S_2O_3^=$) reportedly complexes absorbed SO_2, which aids in inhibiting oxidation of sulfite to sulfate. The reaction is as follows:

   (5) $4HSO_3^- + S_2O_3^= + 2H^+ \rightarrow 2S_2O_6^= + 3H_2O$

   Trithionate is the reaction product.

3. The remainder of the SO_2 may be removed by the reactions shown in the Wellman-Lord process chemistry discussion. The regeneration step is a function of the desired byproduct.

   If elemental sulfur is desired, the reaction is as follows (where hydrogen sulfide can be used as the reductant):

   (6) $HSO_3^- + H^+ + 2H_2S \rightarrow 3S + 3H_2O$

   If SO_2 is desired, the SO_2-rich citrate solution is heated to evolve SO_2 through the following reaction:

   (7) $HSO_3^- + H^+ \overset{\rightarrow}{\Delta} H_2O + SO_2\uparrow$

   The SO_2 may be recovered as liquid SO_2 or may be converted to sulfuric acid in an acid plant; the reactions are shown in the Wellman-Lord process chemistry.

System description--A citrate FGD system can be considered in terms of the following general steps:

- Flue gas pretreatment
- SO_2 absorption
- Absorbent regeneration
- Sulfur product recovery
- Purge treatment

Basically, the equipment in a citrate process unit can be very similar to that in a Wellman-Lord process system. The major differences are that the absorber normally has a packed tower rather than a tray tower absorber and that both the Bureau of Mines and Peabody processes normally use hydrogen sulfide generators to recover the absorbed SO_2 as elemental sulfur. The Flakt process normally recovers the absorbed SO_2 as a concentrated SO_2 gas stream for liquid SO_2 or sulfuric acid production.

As with the Wellman-Lord process, the sodium sulfate decahydrate (Glauber's Salt) that is formed is purged. The rate of purge is a function of the oxygen content of the incoming gas stream.

Operational status and current developments--Two of the three processes have been tested only in pilot facilities. Startup is in process of a 60-MW Bureau of Mines process unit at St. Joe Minerals. Also, the Electric Power Research Institute (EPRI) is currently installing a 1-MW pilot Flakt unit and plans to install a 100-MW Flakt process unit. Table 4.2-30 gives more details regarding several installations of these units.

The St. Joe unit was designed to be a 60-MW demonstration unit. Because the smelter associated with the boiler was shut down, the unit has been operating at 20 to 30 MW; the power produced is fed into the local power grid. The normal startup problems have occurred. Initial results indicate SO_2 removal in the 80 to 90 percent range.[226]

Control cost--The quarterly EPA Industrial FGD Survey reports that the capital costs of the Bureau of Mines (BOM) citrate process demonstration unit (60 MW) at St. Joe Zinc, Monaca, Pennsylvania, is $12.7 million in 1977 dollars, which is $14.8 million in July 1979 terms. This equates to about $250/kW,[227] which is greater than for many other FGD systems; however, this unit is a demonstration unit with a great deal of redundancy built in.

A 1978 publication shows the capital and operating and maintenance cost estimates for the Bureau of Mines citrate process for 500- and 100-MW units with a 2.5 percent sulfur coal as fuel.[228] These estimates are presented in Tables 4.2-31 and 4.2-32.

Energy and environmental impacts--These FGD processes normally have only one purge stream requiring treatment, the sodium sulfate bleed. A

TABLE 4.2-30. CITRATE FGD PROCESS UNITS.

Location	Feed gas origin	Gas volume treated, Nm^3/s (scfm)	SO_2 concentration, %	SO_2 Removal, %	Disposition of SO_2
Magma Copper Co.[231] San Manuel, Ariz. (Bureau of Mines)	Copper smelter	8.5 (300)	1.0-1.5	93-99	Elemental sulfur
Bunker Hill[232,233] Kellogg, Idaho (Bureau of Mines) 4500 hours operation	Lead smelter	28 (1,000)	0.3-1.0 (typically 0.5)	>90	Elemental sulfur
Pfizer[231,234] Terre Haute, Indiana	Coal-fired boiler	57 (2,000)	0.1-0.2	95-97	Elemental sulfur
Boliden Aktiebolag[193] Skelleftehamn, Sweden (Flakt) Operational since Sept. 1976	Copper, lead, and zinc smelters	83 (3,000)	0.5-5.0 (typically 3.0)	90-99	Liquid SO_2
St. Joe Minerals[235] Monaca, Pa. (Bureau of Mines) Early 1980 startup scheduled for this 60-MW power boiler FGD system	Coal-fired power boiler	4,420 (156,000)	0.2	>90 (design)	Elemental sulfur
Tennessee Valley Authority[236] Tuscumbia, Ala. (Flakt) Startup planned for early 1980	Coal-fired power boiler	83 (3,000)	0.2-0.4 (typically 0.24)	90	
Site to be selected (Flakt) Site selection expected in mid-1979	100-MW coal-fired power boiler				

TABLE 4.2-31. CITRATE FGD PROCESS CAPITAL SUMMARY FOR A COAL-FIRED POWER PLANT, 2.5% SULFUR[229]

(thousands of dollars except as shown)

Direct construction cost	500-MW plant	1000-MW plant
Major equipment-- by unit operation		
I - Gas cooling and SO_2 absorption	14,593	29,137
II - Sulfur precipitation	1,050	2,141
III - Sulfur recovery	1,844	3,448
IV - Sodium sulfate removal	350	466
V - H_2S generator	1,647	3,165
VI - Offsites and facilities	162	268
Subtotal	19,656	38,625
Foundations and concrete work	1,436	2,768
Structural steel	997	1,911
Buildings	116	127
Insulation	773	1,357
Instrumentation	955	1,694
Electrical	959	1,717
Piping	5,962	10,935
Painting	154	293
Miscellaneous	657	1,074
Subtotal	12,009	21,876
Total direct construction cost	31,665	60,501
Indirect cost and fee	12,539	23,957
Total capital cost	44,204	84,458
Cost in dollars/kW	88	85

Basis:

New power plant application-- Midwest location.
Indirect cost includes engineering design, construction overhead, taxes, general, and administrative expense.
July 1979 Dollars.

TABLE 4.2-32. CITRATE FGD PROCESS ANNUALIZED OPERATIONAL COST SUMMARY FOR A COAL-FIRED POWER PLANT, 2.5% SULFUR[230]
(first year costs in thousands of dollars except as shown)

Direct operational expense	500-MW plant	1000-MW plant
Chemical feedstocks	1,934	3,874
Utilities	4,822	9,645
Plant operations	259	338
Plant maintenance	311	458
Payroll overhead	139	183
Subtotal direct	7,465	14,498
Indirect expense		
Administrative and overhead	244	225
Insurance	333	637
Subtotal indirect	557	862
Startup costs	975	1,840
Total operational expense	8,997	17,200
Sulfur product credit	(1,360)	(2,721)
Cost (Net operational expense)	7,637	14,479
Mills/kWh (Net operational expense)	2.29	2.17
Interest	4,222	8,068
Depreciation	1,482	2,831
Total expense	13,341	25,378
Mills/kWh	4.02	3.82

Basis:

95 percent plant availability; 80 percent average unit load.
Sulfur credit-- $40/ton.
Maintenance services from a fully staffed power plant maintenance organization
(95 percent nonexempt bonds) SL depreciation-- 25 Years.
Utility financing method expressed in 1978 dollars.

portion of the sodium sulfite in the absorber is oxidized to the sulfate form, which is not an absorbing species.

The Bureau of Mines citrate process is reportedly capable of less than 2 percent oxidation because of the tendency of the citrate process to suppress sulfate formation.[231] Flakt reports that the oxidation of the sulfite absorber liquor at the Boliden smelter is between 0.1 and 0.5 percent of the absorbed SO_2.[220] Flakt believes that oxidation is limited by the chemical reaction rate due to the complex binding ability of the citrate ion. Peabody reports 0.4 to 1.0 percent oxidation from laboratory data, which they attribute to the effect of sodium thiosulfate to inhibit oxidation to sulfate.[224]

The positive side of these citrate processes is that there is a usable, salable produced (sulfur, sulfuric acid, liquid SO_2). There is no large volume of possibly environmentally hazardous sludge that must be stored or otherwise handled and disposed of. The sodium purge product (Glauber's salt) can be salable.

4.2.3.8 Magnesium Oxide Flue Gas Desulfurization--

In operation on boiler flue gases the magnesium oxide (MgO) slurry scrubbing system has demonstrated SO_2 removal efficiencies above 90 percent.[232] Three full-scale utility units have been operated in the United States. Two units were designed for short-term demonstration on oil- and coal-fired utility boilers. A third unit is operating, and four more are in the planning stage.

The MgO process is a proven, regenerable FGD system. Magnesium sulfite is formed in the absorption process and is then dried and calcined to regenerate and recover the MgO for reuse. The same regenerating step produces a gas stream containing 6 to 14 percent SO_2, which can be converted to sulfuric acid, liquid SO_2, liquid SO_3, or elemental sulfur. The process generates no waste streams.

Process chemistry--Fly ash and other particulates are removed from the gas stream before it enters the absorption tower, either by an ESP or a wet scrubber. Removing the particulates minimizes solids buildup and impurities in the regeneration stream.

High-efficiency removal of sulfur oxides from the gas stream requires that the stream be precooled to 40° to 65°C (110° to 150°F) and that the absorbent be highly reactive. Magnesium oxide is an excellent absorbent when it is slaked with water to form magnesium hydroxide, $Mg(OH)_2$ (slaking is hydration, with supplemental heating when needed).

The main absorption reaction takes place between sulfur dioxide (SO_2) and magnesium oxide (MgO) to form either magnesium sulfite hexahydrate ($MgSO_3 \cdot 6H_2O$) or magnesium sulfite trihydrate ($MgSO_3 \cdot 3H_2O$). Some of the SO_2 may react with $MgSO_3$ in the presence of water to form magnesium bisulfite [$Mg(HSO_3)_2$], which then reacts immediately with excess MgO to yield additional $MgSO_3$ (hexahydrate or trihydrate). A portion of the $MgSO_3$ is oxidized to magnesium sulfate ($MgSO_4$). Some of the sulfur trioxide (SO_3) present in the flue gas is absorbed and reacts to form $MgSO_4$. The reactions that occur are as follows:[233-235]

Slurry preparation:

(1) $MgO + H_2O \rightarrow Mg(OH)_2$

SO_2 absorption:

(2a) $Mg(OH)_2 + 5H_2O + SO_2 \rightarrow MgSO_3 \cdot 6H_2O\downarrow$

or

(2b) $Mg(OH)_2 + 2H_2O + SO_2 \rightarrow MgSO_3 \cdot 3H_2O\downarrow$

(3a) $SO_2 + MgSO_3 \cdot 6H_2O \rightarrow Mg(HSO_3)_2 + 5H_2O$

or

(3b) $SO_2 + MgSO_3 \cdot 3H_2O \rightarrow Mg(HSO_3)_2 + 2H_2O$

(4a) $Mg(HSO_3)_2 + MgO + 11H_2O \rightarrow 2MgSO_3 \cdot 6H_2O\downarrow$

or

(4b) $Mg(HSO_3)_2 + MgO + 5H_2O \rightarrow 2MgSO_3 \cdot 3H_2O\downarrow$

(5) $2MgSO_3 + O_2 \rightarrow 2MgSO_4$

SO_3 absorption:

(6) $Mg(OH)_2 + 6H_2O + SO_3 \rightarrow MgSO_4 \cdot 7H_2O\downarrow$

The absorbent slurry is pumped into the upper area of the absorber. After contacting the flue gas and absorbing SO_2, the slurry normally falls into a recirculation tank, in which the magnesium bisulfite formed in the absorber is converted to magnesium sulfite by reaction with fresh magnesium hydroxide from a makeup stream. The slurry in this tank contains primarily magnesium sulfite, sulfate, and hydroxide.

A bleed stream of 5 to 15 percent of the recirculating flow is diverted to the regeneration circuit. The quantity of slurry extracted is theoretically equivalent to the amount of SO_x being removed in the scrubber. This bleed stream is either first routed to a clarifier/thickener for concentration and then to a continuous centrifuge system or is sent directly to the centrifuge. The overflow liquid from the thickener and centrifuge is either pumped back to the main recirculated slurry stream or is used to slake the regenerated or fresh MgO. The underflow (wet cake) from the centrifuge system contains crystals of hydrates of magnesium sulfite/sulfate and some excess magnesium hydroxide.

The wet cake is then conveyed to a direct-contact or fluid-bed dryer, where free and chemically bound water are removed. Typical operating temperatures of a dryer are from 175° to 235°C (350° to 450°F).[235] Although both rotary and fluid-bed dryers can be used, only the rotary kiln type has been used in the three U.S. magnesium scrubbing units.[236]

The following chemical reactions occur in the dryer:[237,238]

(1) $Mg(OH)_2 \rightarrow MgO + H_2O \uparrow$

(2a) $MgSO_3 \cdot 6HO \rightarrow MgSO_3 \cdot 3H_2O + 3H_2O \uparrow$

or

(2b) $MgSO_3 \cdot 3H_2O \rightarrow MgSO_3 + 3H_2O \uparrow$

(3) $MgSO_3 \cdot 6H_2O \rightarrow MgSO_3 + 6H_2O \uparrow$

(4) $MgSO_4 \cdot 7H_2O \rightarrow MgSO_4 + 7H_2O \uparrow$

The anhydrous (water-free) crystals of magnesium oxide (<1 percent), magnesium sulfite, and magnesium sulfate are fed to a calciner (either a rotary or fluid-bed type) to regenerate the MgO and to liberate the SO_2 in the off-gas.[239] The calciner temperatures can range from 670° to 1000°C (1250° to 1800°F) [237,239,240] but caution should be taken not to exceed

850°C (1500°F) for a prolonged period because "dead burning" takes place at and above that temperature. "Dead burned" MgO is characterized by high bulk density (450 to 700 kg/m^3, 28 to 45 lb/ft^3)[241,242] and chemical unreactiveness, which render it ineffective for further use as an absorbent medium.

A reducing atmosphere increases the rate and effectiveness of the calcining operation. In a fluid-bed calciner this can be achieved by limiting the combustion air. The addition of coke in a rotary kiln calciner also generates a reducing atmosphere. Using carbon in the range of 1.5 to 2.0 percent and keeping temperatures between 670° and 725°C (1250° and 1340°F) in the calcining operation will yield a product of low density and high reactivity.[242,243] The following reactions take place in the calciner:[237,239,240,244]

$$(1)\quad MgSO_3 \xrightarrow{\Delta} MgO + SO_2 \uparrow$$

$$(2)\quad 2C + O_2 \rightarrow 2CO \uparrow$$

$$(3)\quad MgSO_4 + CO \rightarrow MgO + CO_2 \uparrow + SO_2 \uparrow$$

The regenerated MgO is stored for later use in the flue gas scrubber slurry system. The off-gas from the calciner is cooled, cleaned, and processed to yield the desired product, usually sulfuric acid.

System description--The MgO process consists of two major parts: the SO_2 scrubbing system and the MgO regeneration system. Major components of the SO_2 scrubbing system are the slurry preparation section, the absorber section, and the bleed stream dewatering section. Major components of the MgO regeneration system are the regeneration section and the sulfur byproduct section.

Before entering the system, the flue gas must be free of particulates and cooled to approximately 53°C (127°F). This can be accomplished in one step by passing the flue gas through a venturi scrubber using circulating water, from which a purge stream is sent to a wastewater treatment unit. A two-step approach to preconditioning is to send the gas through an electrostatic precipitator (ESP) and then through a cooling-humidifying chamber.

Two absorber designs currently have been considered for use in MgO systems. One is the turbulent contact absorber (TCA), which was initially adapted for use with MgO in the United States and has been used for SO_2

removal at a Japanese smelter.[245] The other absorber is the ventri-rod scrubber, used in the United States by United Engineers and Contractors.[246] Figures 4.2-31[247] and 4.2-32[248] are schematic representations of TCA and ventri-rod scrubber installations.

In two demonstration units, venturi absorbers were utilized; however, the constructor (Chemico) believes that these venturi absorbers will not be used on any other utility systems.

An improperly designed absorber is subject to corrosion and erosion caused by the liquid flow, by action of the absorbent itself, and by possible acidic conditions. To reduce costs, absorbers may be constructed of mild carbon steel with an inner protective coating of fiberglass-reinforced polyester (FRP), polyurethane, rubber, or flaked glass.[246] The uncoated sections (internals) of the absorber that have direct contact with the flue gas and absorbent may be made of low-carbon stainless steel, high-nickel alloys, FRP, or other highly corrosion-resistant materials.

The liquid-to-gas (L/G) ratio in MgO systems is in the range of 4.0 to 5.3 liters/m^3 (30 to 40 gal/10^3 ft^3), about half of that used in calcium-based "throwaway" processes.[249] Other advantages are the high solubility of magnesium sulfite, the controllability of slurry composition, the high concentration of crystallization nuclei (for regeneration stream feed), and a short slurry residence time.[250]

Size of an absorber module and the number of modules per system are directly related to the turndown requirement (reduction of throughput), system availability, and gas-liquid distribution. As the boiler load fluctuates, the scrubbing rate should change to maintain optimum performance. One method of accomplishing turndown is to shut down scrubber modules as the load decreases--the more modules in the system, the smoother the transition. Scheduled cleaning and maintenance of absorber modules not in use reduce overall absorber downtime. Operation of multiple absorber modules also permits the use of modules having smaller cross sections, which may promote uniform gas-liquid distribution and improve efficiency. Capacities of absorber modules normally range from 25 to 165 MW.[251]

The mist eliminator, located after the absorber, removes entrained water droplets and slurry from the gas stream. Thus it reduces water loss

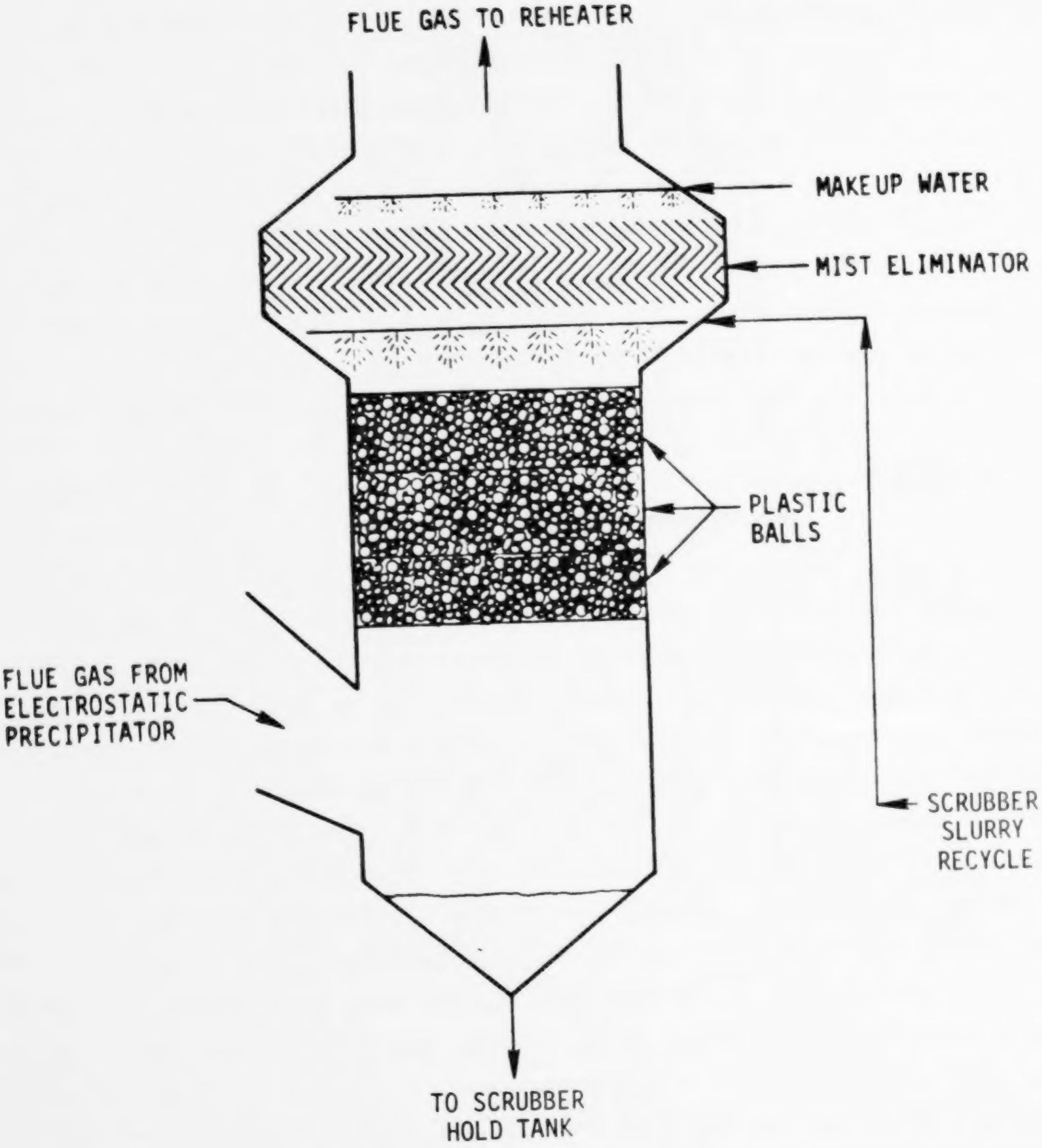

FLUE GAS TO REHEATER
MAKEUP WATER
MIST ELIMINATOR
PLASTIC BALLS
FLUE GAS FROM ELECTROSTATIC PRECIPITATOR
SCRUBBER SLURRY RECYCLE
TO SCRUBBER HOLD TANK

Figure 4.2-31. Typical TCA installation.[247]

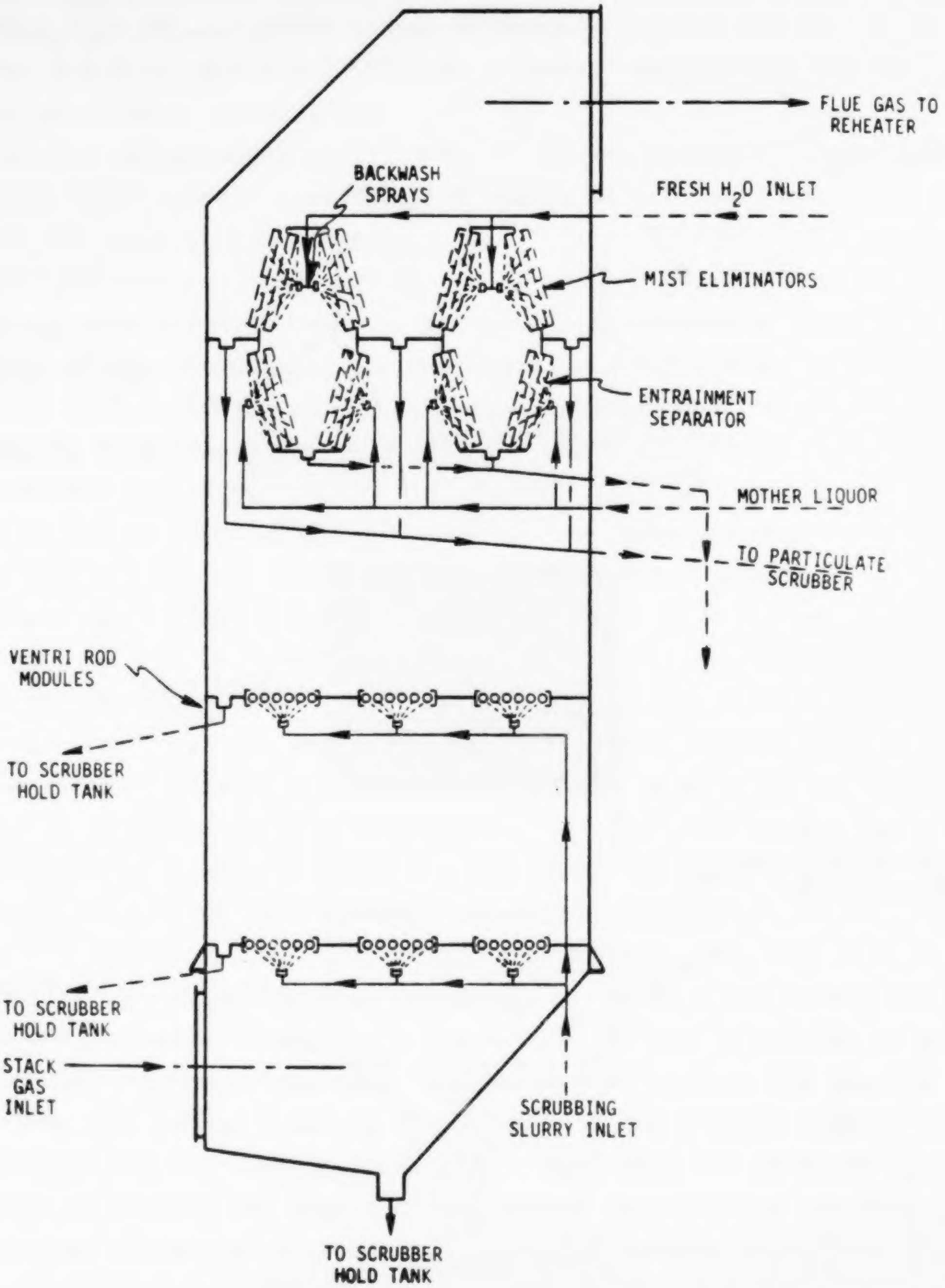

FLUE GAS TO REHEATER
BACKWASH SPRAYS
FRESH H_2O INLET
MIST ELIMINATORS
ENTRAINMENT SEPARATOR
MOTHER LIQUOR
TO PARTICULATE SCRUBBER
VENTRI ROD MODULES
TO SCRUBBER HOLD TANK
TO SCRUBBER HOLD TANK
STACK GAS INLET
SCRUBBING SLURRY INLET
TO SCRUBBER HOLD TANK

Figure 4.2-32. Typical ventri-rod scrubber with mist eliminators.[248]

in the absorption process, reduces corrosion of downstream equipment, and may reduce the need for reheat energy. Most mist eliminators are constructed of stainless steel or FRP, and are located either in the absorber shell immediately above the absorption section or in a separate structure just after the absorber. A mist eliminator is designed to remove the entrained droplets by impaction as the gas is forced to change directions while passing through chevron- or z-shaped sections.

The reheater immediately precedes the exhaust stack. The gas emerging from the SO_2 scrubber often ranges from 48° to 54°C (120° to 130°F) and is saturated with water vapor. Reheating of the gas is generally practiced to prevent water condensation, reduce corrosion, and improve plume dispersion. Reheating of the flue gas can be accomplished by (1) installing a gas or low-sulfur oil burner (2) installing steam coils, (3) using a burner or steam coil to heat ambient air and inject it into the flue gas stream, or (4) bypassing untreated hot flue gas, which is mixed with the treated flue gas.[252]

Usually about 10 percent of the total flow through the absorber recirculation circuit is removed as a bleed stream that is routed to a dewatering section and eventually to the MgO regenerating section. The dewatering equipment is usually a train consisting of a clarifier/thickener, centrifuge, and rotary dryer. Both thickeners and hydroclones (liquid cyclones) can be used as first-stage dewatering units. Although such first-stage treatment may not be required, it improves the centrifuge operation by providing a more consistent feed. The underflow from a typical stainless steel, solid-bowl centrifuge is a wet cake, as discussed under the Process Chemistry Section.[253] The overflow from both the first-stage dewatering and the centrifuge is usually recycled directly to the main slurry recirculation loop. Another possibility is to use this water for slaking the regenerated and makeup MgO before it is returned to the absorber. The underflow of the centrifuge is usually transported by screw conveyor to the dryer.

Most rotary dryers are of the counterflow, incline type. The feed to be dried is introduced at the top and travels downward through the cylindrical, revolving dryer, where it meets the upward moving, hot combustion gases (175° to 230°C, 345° to 450°F). The free and chemically bound water is removed, and the dried crystals of magnesium sulfite and sulfate are then conveyed to storage hoppers. The dryer can be one of the most troublesome areas for continuous operation; problems with dust may also occur.

The composition and temperature of the scrubbing solution are important in determining which of the magnesium sulfite hydrates (hexahydrate or trihydrate) is stable at equilibrium and will eventually be produced as the solid product. For a given solution composition, the hexahydrate is the stable hydrate at temperatures below the transition temperature. Above this temperature, the trihydrate is the stable form. Keeping the temperature of the absorbent medium below this transition temperature promotes maximum growth of the hexahydrate. In pure solutions containing only water and magnesium sulfite, the transition temperature is 41°C (106°F); however, the precipitation of hexahydrate crystals occurs at temperatures higher than 41°C (106°F) in some magnesium oxide scrubbing systems.[254]

The regeneration section consists mainly of a calciner, a particulate collection device, and silos for storage of the regenerated MgO. The calciner can be similar to the rotary dryer or it can be of the fluid bed type.

Selection of an optimum temperature in a fluid bed regenerator represents a compromise. On the one hand high temperatures are needed to reduce the magnesium sulfate to the sulfite form and to ensure the substantially complete decomposition of the sulfate to MgO and SO_2. On the other hand, excessive temperatures will produce dead burned MgO, which is chemically unreactive and thus ineffective for further SO_2 removal. As noted in the discussion of process chemistry, the optimum temperature range for calciner operation is from 670° to 725°C (1250° to 1340°F).[237,239,240] Fluid bed reactors are particularly well suited to precise temperature control. They also allow for precise control of oxygen, which eliminates the necessity of adding oxygen scavengers, such as carbon, to the bed to decompose the magnesium sulfate.[255] Essex Chemical at Newark, New Jersey, uses a fluid bed calciner for regeneration of magnesium sulfite from Philadelphia Electric's Eddystone Station Unit No. 1A.

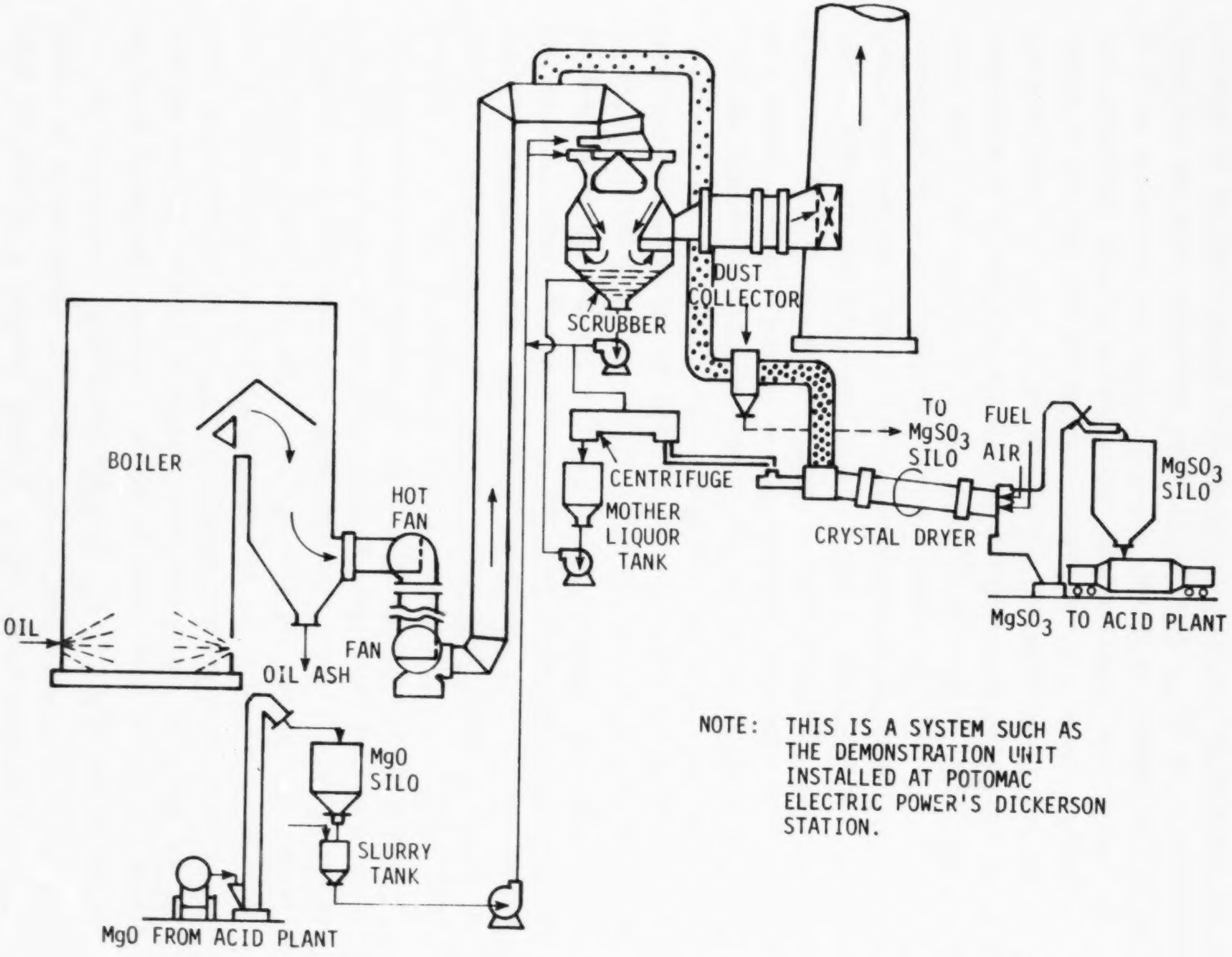
The temperature range is the same as for a rotary calciner. Because control of oxygen cannot be achieved in a rotary calciner, coke normally is added to provide a reducing atmosphere; the total addition of carbon is about 1.5 to 2.0 percent of the feed.[256] Figures 4.2-33 and 4.2-34 show schematic layouts of a venturi scrubber and a rotary calciner (MgO absorption and regeneration system) such as were used at the first two full-scale, demonstration units.[257] Figure 4.2-35 shows a TCA and fluid bed calciner MgO absorption/regeneration system.

The two earliest installations used a rotary kiln to regenerate the MgO. High dust losses in the rotary kiln necessitate the use of a hot cyclone and venturi scrubber to recover the MgO. In a fluid bed reactor, most of the MgO formed goes overhead with the SO_2 and combustion gases, and separation equipment is required.[258]

From the calciner, the regenerated absorbent (MgO) is cooled and stored in silos. Cooling can be accomplished by transporting it pneumatically. An advantage of the MgO system is that the absorbency potential afforded by MgO in a given amount of storage space is roughly double that of a calcium-based absorbent. This effective increase in storage capacity may reduce the effect of an extended outage of the regenerating facilities and possibly improve the availability of the total unit.

Several sulfur byproducts are possible with an MgO regeneration system, the most prominant being sulfuric acid. Other possible products are liquid SO_2, liquid SO_3, and elemental sulfur. Before the gas enters the sulfur byproduct facility, the particulate MgO is removed and stored. The gas is then cooled, usually in a venturi or spray tower. The SO_2 concentration of the gas generally ranges from 8 to 10 percent and the temperature is about 38°C (100°F).[259]

The slurry preparation section links the regeneration circuit to the absorption loop. The bulk (about 95 percent) of the MgO fed to the absorber is regenerated material, the remainder being fresh feed.[260] Heat is sometimes needed to increase the slaking rate of the regenerated MgO.[261,262] Also, maintaining the pH of the main scrubbing slurry stream between 6.8 and 7.5 can increase its absorption capability.[263] The pH is adjusted by controlling the amount of regenerated slurry to be mixed with the main absorbent stream. Mixing is done either in the recirculation tank, which is often located beneath the absorber, or within the absorber.


BOILER
OIL
OIL ASH
HOT FAN
FAN
MgO SILO
SLURRY TANK
MgO FROM ACID PLANT
SCRUBBER
DUST COLLECTOR
CENTRIFUGE
MOTHER LIQUOR TANK
TO $MgSO_3$ SILO
FUEL
AIR
CRYSTAL DRYER
$MgSO_3$ SILO
$MgSO_3$ TO ACID PLANT

NOTE: THIS IS A SYSTEM SUCH AS THE DEMONSTRATION UNIT INSTALLED AT POTOMAC ELECTRIC POWER'S DICKERSON STATION.

Figure 4.2-33. MgO system with a venturi scrubber system.[257]

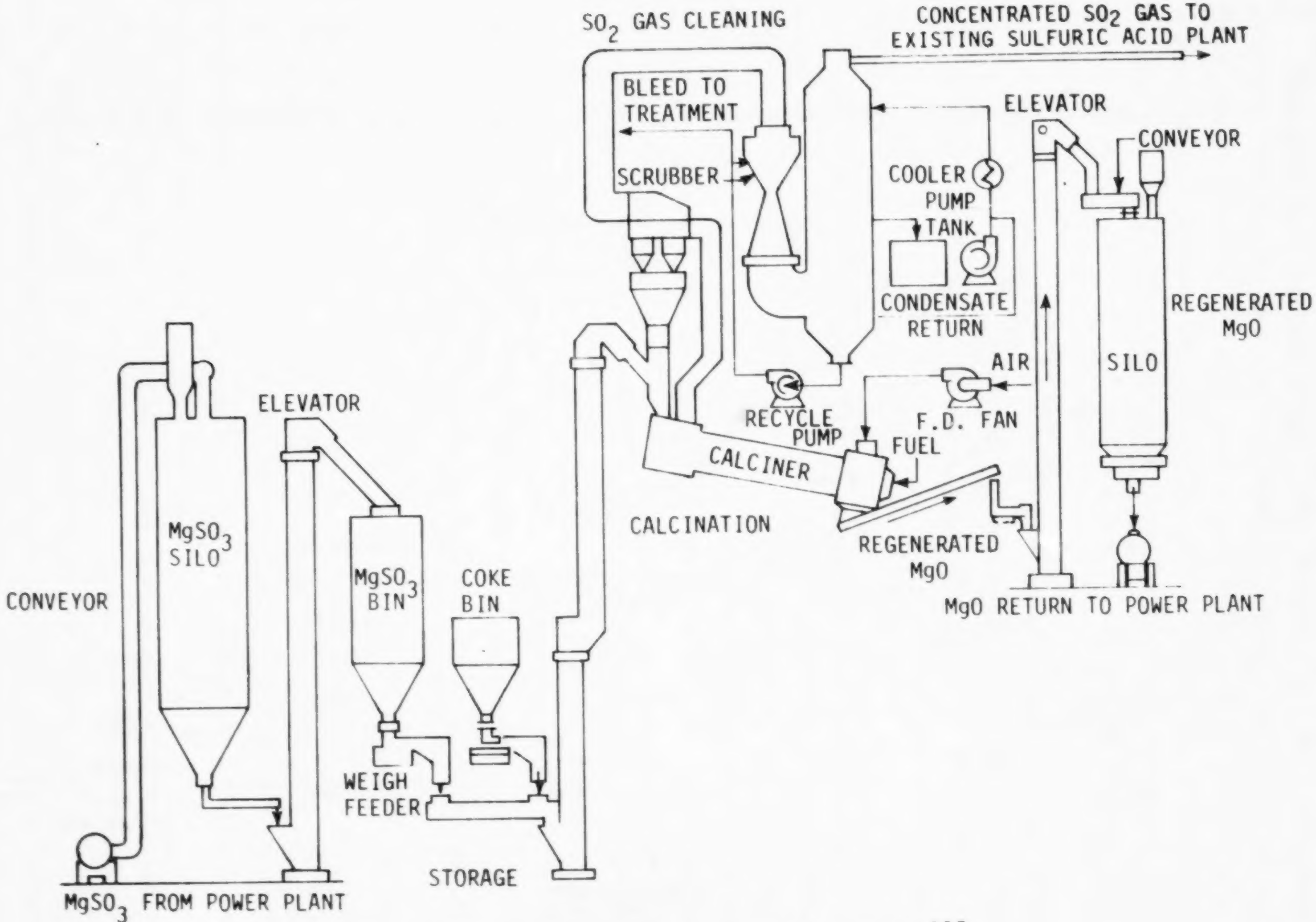

SO_2 GAS CLEANING
CONCENTRATED SO_2 GAS TO EXISTING SULFURIC ACID PLANT
BLEED TO TREATMENT
SCRUBBER
ELEVATOR
CONVEYOR
COOLER
PUMP
TANK
CONDENSATE RETURN
REGENERATED MgO
SILO
AIR
RECYCLE PUMP
F.D. FAN
FUEL
CALCINER
CALCINATION
REGENERATED MgO
MgO RETURN TO POWER PLANT
ELEVATOR
$MgSO_3$ SILO
$MgSO_3$ BIN
COKE BIN
CONVEYOR
WEIGH FEEDER
STORAGE
$MgSO_3$ FROM POWER PLANT

Figure 4.2-34. Rotary calciner MgO regeneration system.[257]

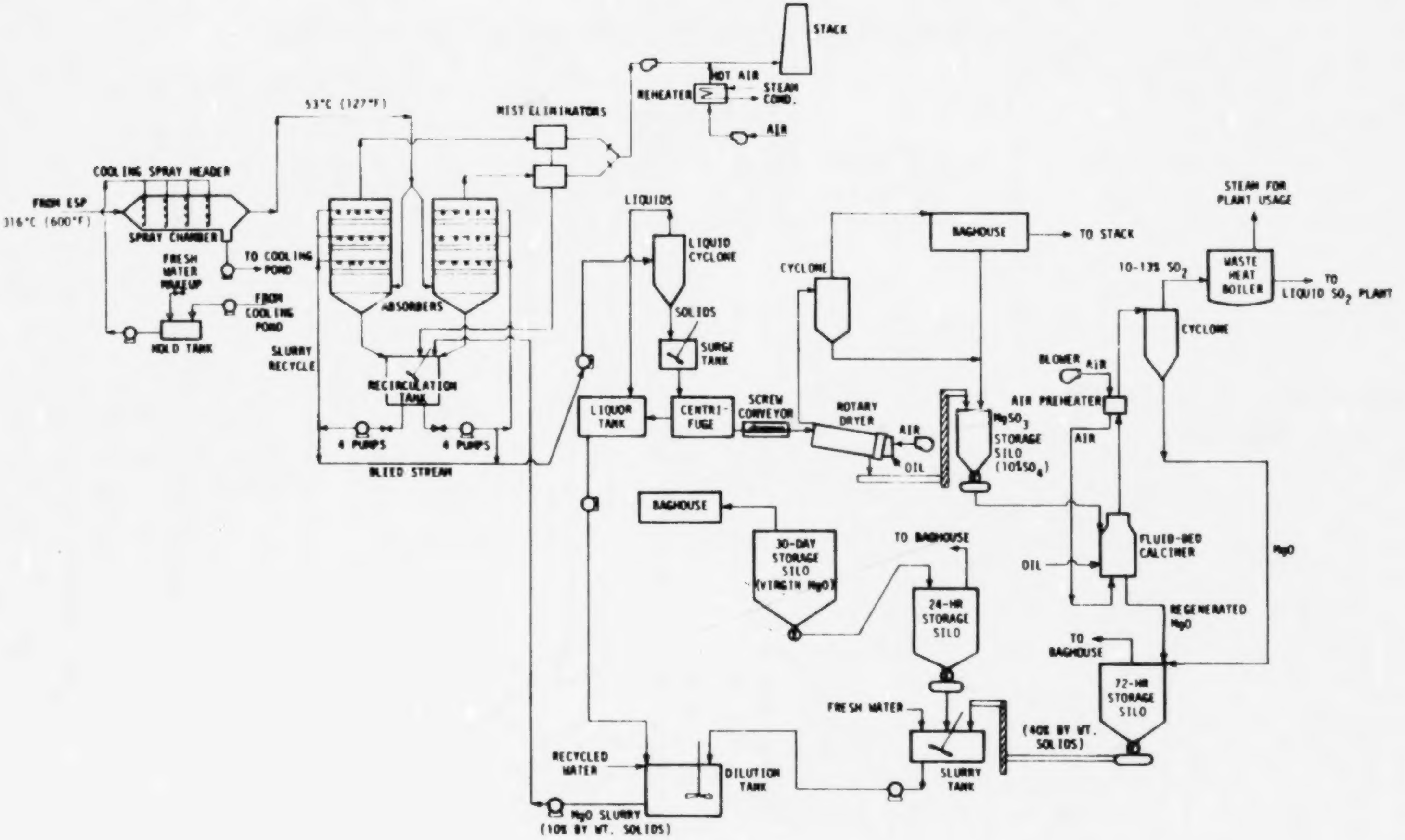

FROM ESP
316°C (600°F)
COOLING SPRAY HEADER
SPRAY CHAMBER
FRESH WATER MAKEUP
TO COOLING POND
FROM COOLING POND
HOLD TANK
53°C (127°F)
ABSORBERS
SLURRY RECYCLE
RECIRCULATION TANK
4 PUMPS
4 PUMPS
BLEED STREAM
MIST ELIMINATORS
REHEATER
HOT AIR
STEAM COND.
AIR
STACK
LIQUIDS
LIQUID CYCLONE
SOLIDS
SURGE TANK
LIQUOR TANK
CENTRI-FUGE
SCREW CONVEYOR
ROTARY DRYER
AIR
OIL
CYCLONE
BAGHOUSE
TO STACK
MgSO3 STORAGE SILO (10%SO4)
BLOWER
AIR
AIR PREHEATER
AIR
CYCLONE
10-13% SO2
WASTE HEAT BOILER
STEAM FOR PLANT USAGE
TO LIQUID SO2 PLANT
FLUID-BED CALCINER
OIL
MgO
REGENERATED MgO
TO BAGHOUSE
72-HR STORAGE SILO
(40% BY WT. SOLIDS)
BAGHOUSE
30-DAY STORAGE SILO (VIRGIN MgO)
TO BAGHOUSE
24-HR STORAGE SILO
FRESH WATER
SLURRY TANK
RECYCLED WATER
DILUTION TANK
MgO SLURRY (10% BY WT. SOLIDS)

Figure 4.2-35. A magnesium oxide FGD system using TCA absorbers and a fluid-bed calciner.

Development and current status--The feasibility of full-scale MgO scrubbing systems has been demonstrated in Japanese and U.S. FGD systems. Three retrofit units in the United States in the 95- to 150-MW range have demonstrated 90 percent SO_2 removal during individual SO_2 removal test runs on both coal- and oil-fired boilers. These and planned MgO units are listed in Table 4.2-33.[264,265] All the MgO systems installed to date have been retrofits.

Scaling or plugging in the scrubber has not been a problem in magnesia slurry scrubbing systems. Venturi or venturi-type scrubbers (single-stage, double-stage, or ventri-rod types) have been used on all U.S. plants to date, and SO_2 removal efficiencies of over 90 percent during individual SO_2 removal test runs have been obtained.[266]

Some common problems to the U.S. units upon startup were exemplified at Boston Edison. Most of the problems were related to materials handling and resulted from characteristics of the solids formed in the scrubbing loop. The production of small (10 to 15 μm) magnesium sulfite trihydrate crystals rather than the larger hexahydrate crystals caused the centrifuge cake to retain excessive amounts of unbound moisture. The operational chemistry of the absorber is the controlling factor in crystal growth. The magnesium sulfite trihydrate crystals are flat platelets, which form structures that can trap unbound moisture. Extraction of this "trapped" water with a centrifuge is difficult. The wet cake can readily cause buildup in the rotary dryer or in solids handling equipment, with associated plugging problems.

The problems at Boston Edison were solved by several operating and design modifications, which included changing the dryer to function as a granulator and adding hammers to loosen materials adhering to the dryer shell. The granulator discharge was screened and sent through lump breakers to crush the oversize agglomerated granules of magnesium sulfite. The dryer off-gas was sent to the SO_2 absorber to prevent high dust losses.

Other problems in MgO units have occurred in the calcining system. Formation of the very fine trihydrate crystals in an oil-fired power plant application resulted in dusting problems in the rotary calciner. Operators of the Essex Chemical facility at Rumford, Rhode Island, eliminated the dusting in the calciner by use of a cyclone followed by a venturi scrubber to remove all the MgO fines from the gas. Leakage of air into the calciner

TABLE 4.2-33. OPERATING AND PLANNED MAGNESIA SCRUBBING UNITS ON U.S. POWER PLANTS AS OF SEPTEMBER 1978[a,b]

Utility company, Power station	Size of FGD unit, MW	Process vendor	Fuel type and sulfur content, %	SO_2 recovery, %	Startup date; status
Boston Edison Mystic No. 6	150	Chemico	Oil, 2.5	90	Startup in April, 1972; test program completed in June 1974; not currently operational
Potomac Electric and Power, Dickerson No. 3	95	Chemico	Coal, 2.0	90	Startup in September 1973; test program completed in September 1975; not currently operational
Philadelphia Electric Co., Eddystone No. 1A	120	United Engineers	Coal, 2.5	95	Startup in September 1975; currently operational
Philadelphia Electric Co., Eddystone No. 1B	240	United Engineers	Coal, 2.5		Letter of intent signed; startup date June 1980
Philadelphia Electric Co., Eddystone No. 2	336	United Engineers	Coal, 2.4		Considering FGD; startup projected June 1980
Philadelphia Electric Co., Cromby	150	United Engineers	Coal, 3.0		Considering FGD; startup projected June 1980

[a] All units are retrofit installations.

[b] Sources: References 264 and 265.

was a problem because the reduction of magnesium sulfate requires a reducing atmosphere. Installation of new seals on the rotary calciner corrected the problem.[267]

Other problems have been erosion and corrosion in the carbon steel recirculating slurry piping. The use of rubber-lined pumps, valves, and piping is considered a practical solution.[261,262] The recirculation pumps also have withstood corrosion through the use of 316 stainless steel impellers.[268]

Notwithstanding these problems, some positive observations are also noted. The chemical and mechanical performance of the scrubber was better than expected at Boston Edison. In the absorber, no internal plugging occurred and the polyester lining was in good condition after 2 years of intermittent operation.

The major problems encountered at Potomac Electric Power's Dickerson Station were related to materials handling. The major equipment items (scrubber vessel, thickeners, centrifuge, and dryer) all performed well. Major problems were encountered, however, with construction materials for handling systems. Carbon steel pipe and slurry pumps were found to be inadequate against the corrosive/erosive properties of the slurry. Individual pump suction and discharge lines were necessary since leaks in pipes at or after a header could make installed spare pumps useless. The designs of the centrifuge discharge hopper, weigh belt feeders, and the dry magnesium sulfite bucket elevator were improved.[269]

Proper feeding of magnesium oxide to the slurry system became a problem, because of plugging in the mix tank and suction lines to the feed pumps. Later, there were difficulties with the proper slaking of regenerated MgO. The final solution to both problems was the installation of a steam-sparged, agitated premix tank/slaker to promote dissolution.[269]

Various rods, bellows, hangers, etc., corroded in the reaction vessel. It was found that the wrong materials had been used, particularly 304S.S. instead of the specified 316S.S. The proper materials were used to replace the corroded parts and this problem was solved. Corrosion and erosion were severe in the recirculating piping of both first- and second-stage scrubber slurry. Fiberglass reinforced polyester (FRP) and epoxy were used to make repairs. For long-term commercial use, however, rubber-lined piping should be specified.[269]

When the calciner was used, it was discovered that magnesium sulfite from Dickerson Station was predominantly hexahydrate, whereas that obtained from Boston Edison's Mystic Station was mostly trihydrate. This necessitated additional testing, to determine the proper operating parameters (temperature and feed rate) for calciner operation.[269]

The bucket elevator conveying the dried magnesium sulfite to the storage silo tended to overload and trip. The problem was traced to the discharge chute from the centrifuge, where wet magnesium sulfite cake tended to hang up and then break off in large chunks. Modifications to the discharge of the centrifuge outlet hopper and installation of larger buckets for the sulfite elevator helped overcome this.[269]

Problems affecting the centrifuge included buildup of material or wear inside the centrifuge, and changes in the physical/chemical form of the magnesium oxide. Use of washout ports and hardened steel surfacing helped remedy this.[269]

The magnesia scrubbing process has been used on a commercial scale at three locations in Japan, as summarized in Table 4.2-34. These units have demonstrated SO_2 recovery of over 90 percent. In the Japanese operations the large hexahydrate crystals were obtained at both the Onahama and Mitsui installations. There were no problems in the filtration and drying steps, as occurred at Boston Edison. The oxidation of sulfite to sulfate in the absorber at Mitsui was only 7 to 10 percent, or half as much as was reported at Boston Edison.

Control costs--The capital costs of the existing systems have varied greatly because of the different types of equipment used and the quantities of flue gas handled at each installation. One report lists the costs of the three units in the United States. With all prices escalated to July 1979, the capital costs, operating and maintenance costs (both total and per kilowatt-hour), and the FGD system capacities are shown in Table 4.2-35.

TABLE 4.2-34. OPERATING MAGNESIA SCRUBBING UNITS ON JAPANESE POWER PLANTS AS OF 1978 [264,270]

Company location	Type of plant	Size of FGD unit, MW	Process vendor	Flue gas SO_2 content, ppm	SO_2 recovery, %	Byproduct	Startup date; status
Onahama Smelter Onahama, Japan	Copper smelter	27	Onahama-Tsukishima	15,000-25,000	99.5	H_2SO_4	Startup in December 1972; plant shut down because of energy conservation and abundance of sulfuric acid
Mitsui Mining Hibi, Japan	H_2SO_4	26	Mitsui-Mining	1,500-2,000	90	H_2SO_4	Startup in October 1971; plant shut down because of energy conservation and abundance of sulfuric acid
Idemitsu Kosan Chiba, Japan	Claus unit and boiler	160	Chemico-Mitsui		95	Sulfur	Startup in 1975; currently operational

TABLE 4.2-35. COSTS ASSOCIATED WITH THREE MAGNESIUM OXIDE UNITS[271]

	Capital costs, $/kW	Operations and maintenance cost, Total annual, mills/kWh	FGD system capacity, MW
Boston Edison (Mystic)	55	4.6[a]	150
Potomac Electric (Dickerson)	109	6.3[b]	95
Philadelphia Electric (Eddystone)	111	7.5[a]	120

[a] Estimation.
[b] Based on questionnaire.

Others have taken a more general approach to costing MgO systems. One report lists a variety of costs for different conditions of input to the absorption unit.[215] Table 4.2-36 is a reduced version of these costs, showing 3.5 percent sulfur coal as the fuel and assuming 90 percent SO_2 removal efficiency. Figures 4.2-36 and 4.2-37 depict these costs and similar ones for 7.0 percent sulfur coal at the same SO_2 removal efficiency. The total annual operating costs include both operation and maintenance costs and fixed charges.

Another source quotes $75.8 million as the capital costs of an MgO system for a coal-fired boiler burning 3.5 percent sulfur coal; it is assumed that regeneration will be done off site. This source also lists the total annual cost as $10.4 million, which includes transport of the magnesium sulfite to a regeneration site and fixed costs of 14.9 percent of total investment.[272] (These costs are also escalated to July 1, 1979.)

Capacity and energy penalties are also considered in comparing costs of FGD systems. A capacity penalty is calculated by comparing the total electrical requirements of the FGD system with the total original output of electricity from the power plant, before the FGD was on-line. This number is usually expressed as a percentage, as it is in Table 4.2-37.

TABLE 4.2-36. COSTS OF AN MgO ABSORPTION SYSTEM AT 90% REMOVAL EFFICIENCY[a]

Boiler capacity	COSTS				
	Capital,[b] $/kW	Operating and maintenance, mills/kW	Fixed, mills/kW	Total annual, mills/kW	Capital,[b] $ 10^3
25 MW	408.80	13.99	17.56	31.55	10,220
100 MW	329.50	8.15	14.15	22.30	32,950
200 MW	216.95	5.63	9.32	14.95	43,390
500 MW	162.42	4.57	6.98	11.55	81,210
1000 MW	136.68	3.85	5.37	9.72	136,680

[a] Adapted from Reference 215.

[b] Capital costs are adjusted to July 1, 1979.

Note: Data based on use of 3.5% sulfur coal.

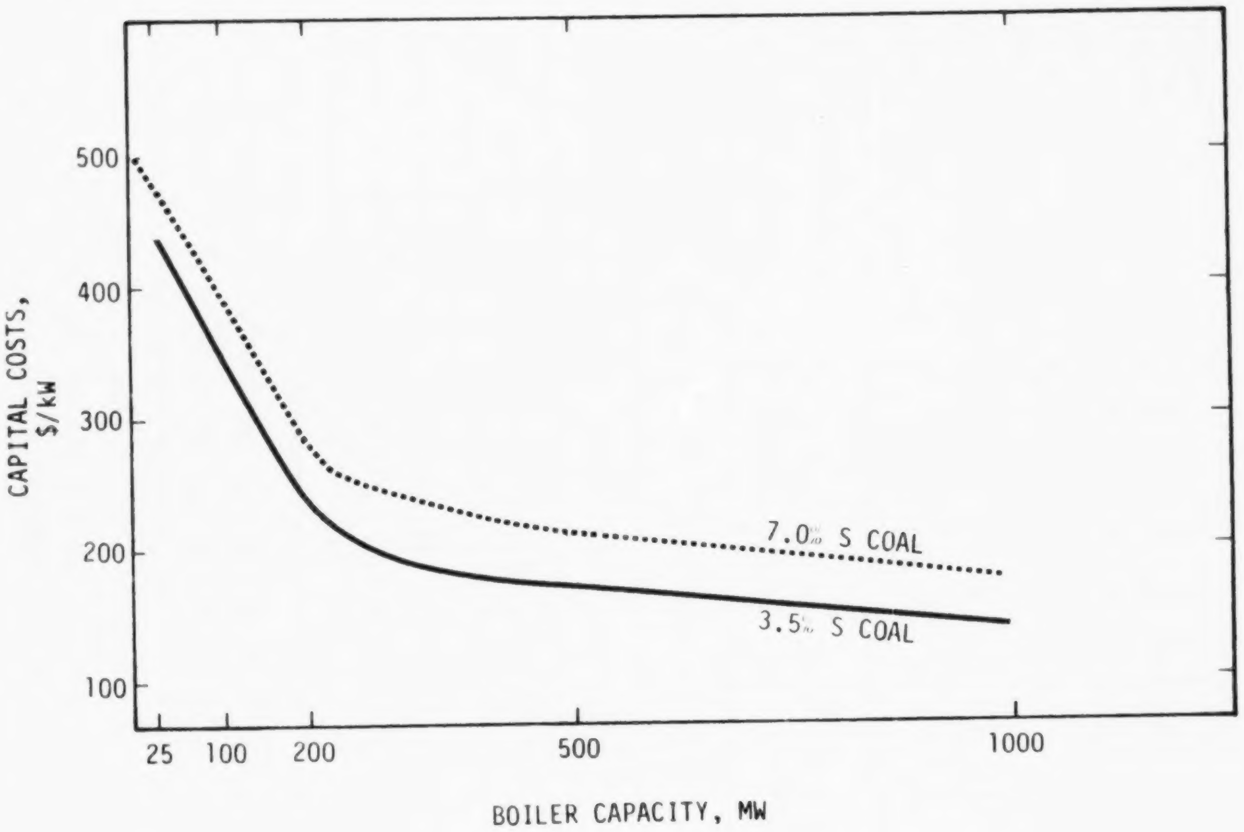


Figure 4.2-36. Capital costs of MgO FGD systems given 90% SO_2 removal efficiency.[215]

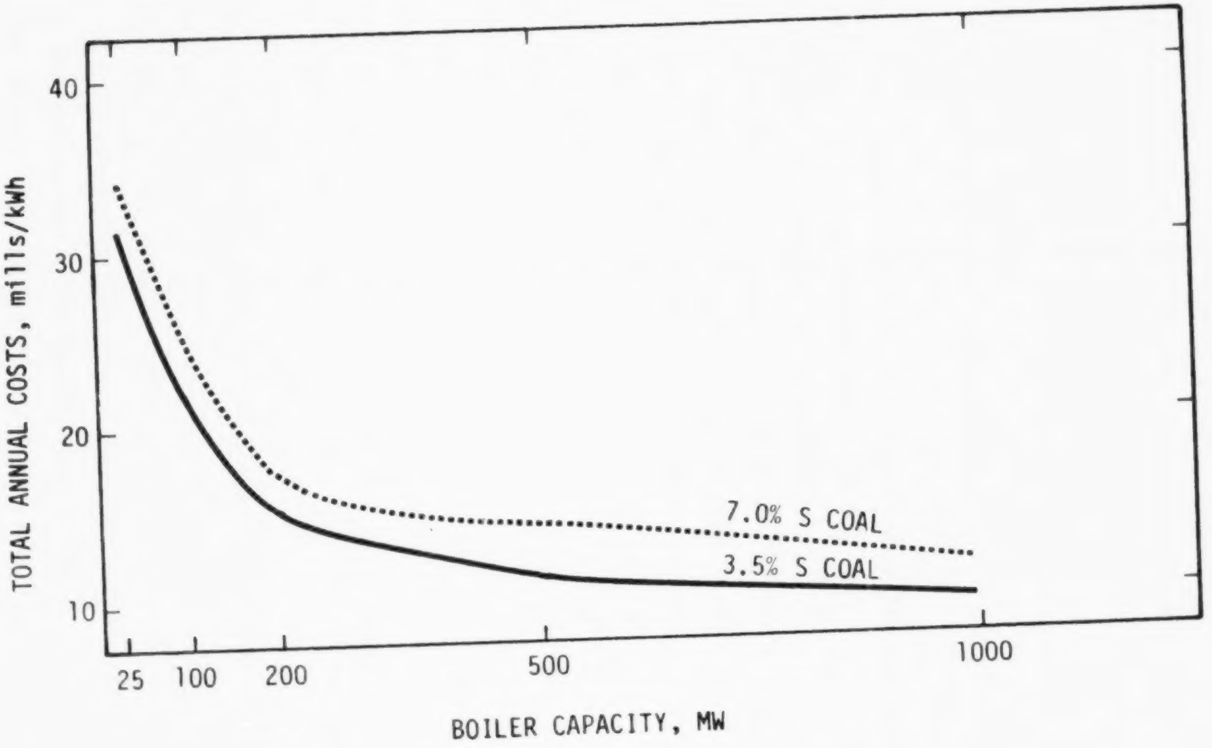


Figure 4.2-37. Total annual operating costs for MgO FGD systems given 90% SO_2 removal efficiency.[215]

TABLE 4.2-37. CAPACITY AND ENERGY PENALTIES FOR VARIOUS FGD AND FUEL TYPES.[273]

Coal type, % sulfur	Capacity, MW	Lime		Limestone		Mag-Ox		Dual alkali		Wellman-Lord	
		Capacity penalty	Energy penalty	Capacity penalty	Energy penalty	Capacity penalty	Energy penalty	Capacity penalty	Energy penalty	Capacity penalty	Energy penalty
Eastern, 3.5	25	3.03	4.67	3.03	4.67	3.80	5.44	3.03	4.67	3.80	9.72
	100	2.91	4.59	2.91	4.59	3.64	5.32	2.91	4.59	3.64	9.64
	200	2.76	4.41	2.76	4.41	3.45	5.10	2.76	4.41	3.45	9.41
	500	2.67	4.30	2.67	4.30	3.34	4.98	2.67	4.30	3.34	9.29
	1000	2.60	4.25	2.60	4.25	3.25	4.90	2.60	4.25	3.25	9.22
Eastern, 7.0	25	3.03	4.67	3.03	4.67	3.80	5.44	3.03	4.67	3.80	13.40
	100	2.91	4.59	2.91	4.59	3.64	5.32	2.91	4.59	3.64	13.24
	200	2.76	4.41	2.76	4.41	3.45	5.10	2.76	4.41	3.45	13.02
	500	2.67	4.30	2.67	4.30	3.34	4.98	2.67	4.30	3.34	12.90
	1000	2.60	4.25	2.60	4.25	3.25	4.90	2.60	4.25	3.25	12.83

Note: Penalties are expressed as a percentage of the gross electrical generation.

Energy penalties are related closely to capacity penalties. Both are calculated by finding the total electrical usage of the FGD system. The energy penalties, however, also include any other type of energy that the FGD system might need to operate. Other energy users could be a flue gas reheater, a slaking tank, or any steam sparging unit. Table 4.2-37 also lists energy penalties as percentages of the gross electrical generation. The values listed are for purchasing the additional electrical power needed rather than building to provide extra capacity.

4.2.3.9 Adsorption--

The phenomenon of adsorption can be used in collecting SO_2 from flue gas; when the molecules of SO_2 are brought into contact with a solid adsorbent, they adhere to the surface of the adsorbent material. Among several materials that have been investigated for use as SO_2 adsorbents, activated carbon has been investigated most intensively.

The Reinluft process, developed in Germany in the late 1950's, was the first major carbon adsorption system. Several test units were operated between 1959 and 1968.[274] Bergbau Forschung later conducted pilot plant studies at the Welheim power plant in West Germany,[275] and together with Foster Wheeler offer a dry adsorption system utilizing activated coke (char) as the adsorbent.[276] This system is known as the Bergbau Forschung/Foster Wheeler (BF/FW) process. In the mid-1970's, demonstration plants were installed at the Kellerman power plant in Lünen, West Germany, and at the Scholz steam plant of the Gulf Power Company in Sneads, Florida. In Japan, the Kansai Electric Power Company and Sumimoto Shipbuilding and Machinery Company jointly developed a similar carbon adsorption system. Following pilot plant tests in 1969, they constructed a demonstration unit at the Sakai Port power station of Kansai Electric. Although this unit has been operating since 1972, very little operating information is available.[277,278] The discussion that follows therefore deals chiefly with the BF/FW process.

The demonstration plant in Lünen treats a portion of the flue gas from a 350-MW boiler (150,000 Nm^3/h, or 88,275 scfm--about a 35-MW equivalent). The Scholz demonstration unit treated 40.4 m^3/s (85,600 acfm) of flue gas, roughly equivalent to 20 MW.[279] The process includes regeneration of the adsorbent for reuse; the regeneration step produces a concentrated stream of SO_2, which is reduced to elemental sulfur. The Lünen plant utilized a modified Claus unit to reduce the SO_2 to elemental sulfur, and the Scholz plant demonstrated Foster Wheeler's proprietary RESOX reduction process.

Pilot plant tests have shown that the BF/FW process can remove 97 percent of the SO_2 from flue gas streams and may also remove some particulate, NO_x, and hydrocarbons.[280] At inlet loadings ranging from 0.49 to 3.20 g/Nm^3 (0.2 to 1.3 gr/scf), particulate removal has been reported to range from 93 to 96 percent.[281] It is suspected that char abrasion contributes particulate to the flue gas at the Scholz plant.[282] At any rate, particulate removal in the adsorption section of the system could compromise SO_2 removal efficiency. Foster Wheeler reports that NO_x removal efficiency for the BF/FW process ranges from 40 to 60[283] percent. Tests at the Scholz plant indicated that NO_x removal ranges from 17 to 50 percent with an average of about 20 percent.

Process description--The BF/FW system consists of adsorption, regeneration, and reduction steps, occurring as follows:[284]

Adsorption	(1)	$SO_2 + 1/2\ O_2 \rightarrow SO_3$
	(2)	$SO_3 + H_2O \rightarrow H_2SO_4$
Regeneration	(3)	$H_2SO_4 \rightarrow SO_3 + H_2O$
	(4)	$2SO_3 + C \rightarrow CO_2 + 2SO_2$
Reduction	(5)	$SO_2 + C \rightarrow CO_2 + S$

In the first two reactions, SO_2 collects on the surface of the adsorbent, is oxidized, and is transported to the inner pores as sulfuric acid, allowing more SO_2 to be adsorbed on the surface. Eventually the adsorption ceases and the adsorbent must be regenerated. In the regeneration steps, the adsorbent carbon is heated to about 650°C (1200°F) in an inert atmosphere. The adsorption process is thereby reversed; SO_3 is released and is reduced to SO_2. In the reduction phase the concentrated stream of SO_2 is reduced to elemental sulfur in a RESOX unit. Elemental sulfur and ash are the only byproducts of the system.[285,286]

Figure 4.2-38 is a simplified process flow diagram of the BF/FW system.[287] After passing through particulate collection equipment, boiler flue gas enters the adsorber(s). The gas passes horizontally through a vertical column of adsorbent in a crossflow, while the activated char (adsorbent)

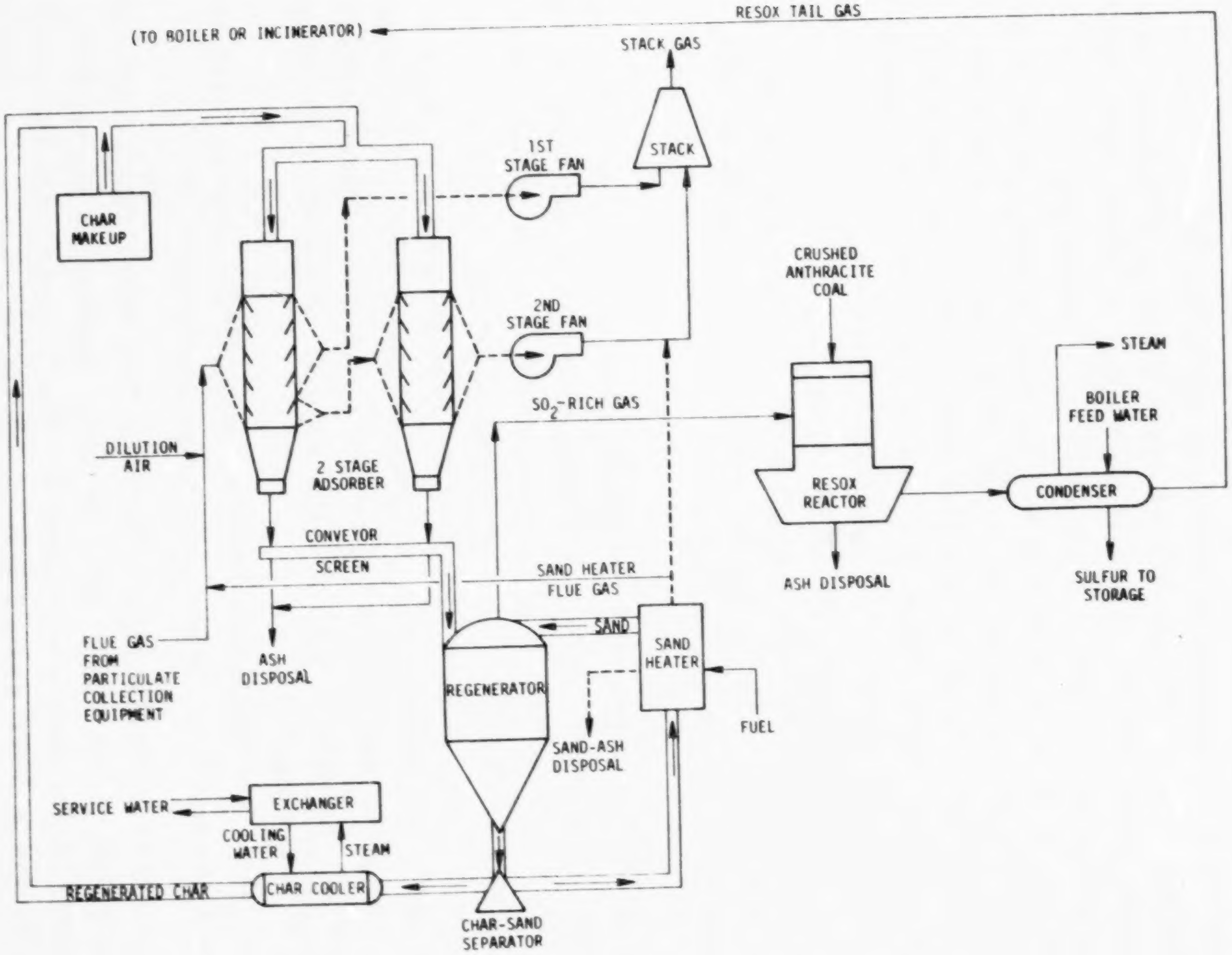

RESOX TAIL GAS
(TO BOILER OR INCINERATOR)
STACK GAS
STACK
1ST STAGE FAN
2ND STAGE FAN
CHAR MAKEUP
CRUSHED ANTHRACITE COAL
STEAM
BOILER FEED WATER
CONDENSER
SULFUR TO STORAGE
SO_2-RICH GAS
RESOX REACTOR
ASH DISPOSAL
DILUTION AIR
2 STAGE ADSORBER
CONVEYOR
SCREEN
SAND HEATER FLUE GAS
SAND
SAND HEATER
FUEL
FLUE GAS FROM PARTICULATE COLLECTION EQUIPMENT
ASH DISPOSAL
REGENERATOR
SAND-ASH DISPOSAL
SERVICE WATER
EXCHANGER
COOLING WATER
STEAM
REGENERATED CHAR
CHAR COOLER
CHAR-SAND SEPARATOR

Figure 4.2-38. BF/FW adsorption process.[287]

moves downward in plug flow. Vibratory feeders control the rate of char flow, which depends upon the quantity of SO_2 in the flue gas. Gas passing through the lower half of the adsorber may be routed to a second-stage adsorber unit. The cleaned flue gas passes through a fan at the adsorber discharge before it is exhausted through the stack.[288,289]

The spent char, in the form of small pellets, is conveyed to the regenerator, where the temperature of the char is raised to 650°C (1200°F) by mixing it with hot sand at 815°C (1500°F). The sand and char are then separated by a vibrating screen deck. The char is spray-cooled to about 120°C (250°F) and returned to the top of the adsorber by bucket elevators. Makeup char is added to replace the char that is lost in the regenerator. A fluidized-bed sand heater reheats the sand to 815°C (1500°F). Bleed-off of the sand removes ash and small char particles.[290-292]

The regenerator off-gas (25 to 40 percent SO_2 by weight) enters the RESOX process in counterflow to a mass flow of crushed anthracite coal. The SO_2 is reduced, and molten elemental sulfur is recovered in an inclined shell-and-tube condenser. The sulfur is stored in liquid form in an insulated tank.[293]

The operating problems with the demonstration units at Scholz and Lünen are primarily mechanical rather than chemical as in other types of FGD systems.[294,295] At Scholz, poor char distribution in the adsorber caused imbalances in the bed level. This imbalance reduced SO_2 removal efficiency and created hot spots in the adsorber that hampered cooling of the char. Char consumption was about 5 times the expected level.[295,296] In addition, improper design of the char/sand separator and hot-sand bucket elevator caused frequent outages,[297] and the sulfur condensor of the RESOX system was susceptible to plugging.[295]

Operation of the process at Lünen has been more successful following initial problems with fans, dampers, and bucket elevators.[298,299]

Energy and environmental impacts--Although the BF/FW process does not include reheating of the exhaust gas, the energy requirements may be as high as 10 percent of the power plant output.[293] Table 4.2-38 lists the energy requirements for a BF/FW process that cleans the flue gas from a 500-MW power plant firing 3.5 percent sulfur coal.[300]

TABLE 4.2-38. ENERGY REQUIREMENTS OF THE BF/FW SYSTEM FOR A 500-MW PLANT[300]

Process section	Coal (bituminous), GJ/h (10^6 Btu/h)	Coal (anthracite), GJ/h (10^6 Btu/h)	Electricity consumed, MW
Adsorption			6.4
Regeneration	220.5 (210)		1.3
Reduction		168 (160)	0.1
Total	220.5 (210)	168 (160)	7.8

Since the BF/FW process is a regenerable system, the environmental effects are minimal in comparison with those generated by throwaway FGD systems. Sulfur, dry fly ash, small amounts of char fines, sand, and cooling water are the only effluents.[301] Gases from the sulfur condenser and sand heater can contain various sulfur compounds and may not be suitable for release. These gases can be recycled to the adsorber.[302]

Cost--The only applications of the BF/FW system to date are the demonstration units. Thus, the quantity of cost information is extremely limited and its accuracy is not known. Table 4.2-39 presents capital and operation costs for a 500-MW unit.[303-305] Data from the Scholz Station indicate that operating costs may be higher than predicted because of the high rates of char consumption in the regenerator and because mechanical maintenance costs are approximately 50 percent greater than those incurred with other prototype systems tested.[306]

4.2.3.10 Dry Removal Processes--

The term "dry removal process" designates any FGD process from which a dry product directly results. There are currently three major types of dry FGD systems being developed today: spray drying, dry injection, and combustion of fuel/limestone mixtures. Of these three systems, spray drying is currently the only one being developed on a commercial scale.[307] Table 4.2-40 summarizes the primary features of these three main types of dry FGD systems.

Dry removal offers various advantages over wet scrubbing. Dry removal systems do not require the sludge handling equipment that many wet scrubbers need. Scaling and plugging, common problems at the wet/dry interface in wet scrubbers, are avoided in dry removal units because only a dry product contacts the walls. Whereas wet systems often use special materials of construction or coatings to prevent corrosion and erosion, the vessels and duct work of dry systems can be made of low-carbon steel. Dry removal units require less manpower to operate than wet scrubbers and can respond more quickly to fluctuations in SO_2 levels. Because dry systems operate with relatively low pressure drops through the absorption system and with smaller volumes of spent absorbent, the operating expenses that wet systems incur because of high pressure drops and greater volumes of spent absorbent can be

TABLE 4.2-39. CAPITAL AND OPERATING COSTS OF A 500-MW BF/FW SYSTEM (MID-1979 BASIS)

Coal sulfur content, % or plant	Capital cost, 1000 $	Capital cost, $/kW	Operating cost, $/yr
0.9[303]	16,410	32.82	1,438,000[a]
4.3[303]	32,825	65.65	4,673,000[a]
3.5[304]			
Adsorption			829,000
Regeneration			5,366,000
Reduction			1,055,000
Total			7,250,000[b,c]
Lünen, West Germany,[305] 49 MW	3,016	61.55	1,219,000[d]
Sholz, 20 MW[305]			
Low-sulfur coal	616-862	30.80-43.10	
High-sulfur coal	1,724-1,847	86.20-92.35	

[a] Based upon 60 percent capacity factor, 1.05×10^7 J/kWh (10,000 Btu/kWh) heat rate, and coal with a heating value of 2.78×10^7 J/Kg (12,000 Btu/lb).

[b] Based upon 60 percent capacity factor and 90 percent sulfur removal.

[c] Raw material and utility costs only.

[d] Includes fixed costs.

TABLE 4.2-40. SUMMARY OF KEY FEATURES OF DRY FGD SYSTEMS[308]

Process type	Spray drying/ particulate collection	Dry injection/ particulate collection	Combustion of coal/ limestone fuel mix
Unique design features	Employs a spray dryer equipped with atomizers to spray sorbent solution or slurry into incoming SO_2 laden flue gas The spray dryer is coupled with a baghouse (or possibly ESP) to provide collection of fly ash and entrained product solids	Pneumatic injection of dry alkali sorbent into a flue gas stream with subsequent particulate collection Injection point varies from immediately after the boiler to just upstream of the collection device (Baghouse or ESP) A baghouse is usually employed as considerable SO_2 removal occurs across the filter cake collected in the bag surface	The most promising technologies in this area appear to be 1) combustion of a coal/limestone pellet in a spreader stoker boiler, and 2) combustion of a coal/limestone fuel mixture in a low-NO_x burner The lower adiabatic flame temperature resulting from the two-stage combustion scheme employed in both technologies appears to increase the available limestone reactivity
Reagent(s) used	Sodium carbonate, lime, trona ($NaCO_3$, $NaHCO_3$, $2H_2O$), and limestone have all been tested Planned commercial systems will use sodium carbonate or lime	Sodium-based alkalis sodium carbonate, sodium bicarbonate, trona, and nahcolite (60-70% $NaHCO_3$) Lime and limestone have been investigated, but both require 600+°F flue gas for significant SO_2 removal	Limestone (Pellet also requires some type of binder)
Ranges of Reagent Utilization	80 to 100% for sodium-based alkalis. 30 to 50% for lime on a "once-through" basis. 80 to 90% for lime with partial recycle of product solids. 20% or less for limestone Reagent utilization is a strong function of the outlet temperature of the gas; utilization increases as the dryer outlet temperature of the gas approaches its adiabatic saturation temperature.	(Baghouse systems) 40 to 60% for nahcolite, sodium bicarbonate at highest SO_2 removal conditions. 20% or less for limestone even at high flue gas temperature. Utilization increases at higher gas temperatures and is a function of sorbent feeding method	Ca:S ratios of 7:1 have been used in coal/limestone pellets while a 3:1 ratio was used for the low-NO_x burner tests.
Ranges of SO_2 removal	(For inlet SO_2-1000 to 2000 ppm) 80 to 90% for sodium-based alkalis 45 to 60% for lime on a "once-through" basis. 80 to 85% for lime with partial recycle of product solids Less than 30% for limestone[a]	60 to 90% for sodium-based alkali systems depending on stoichiometric ratio, flue gas temperature, and method of feeding. 90% removals have been achieved with nahcolite at 290°F temperatures 20 to 30% for limestone at high temperatures (600+°F)	Coal/limestone pellets captured 75 to 80% of the available sulfur in the fuel. Preliminary results in tests with low NO_x burners indicate that 80% retention is achievable
Particulate removal	Both baghouses and ESP's have consistently achieved 99+% removal of entrained product solids and fly ash Baghouses have the advantage of providing for additional SO_2 removal across the filter cake that collects on the fabric surface However, some reports claim it is possible to more closely approach the adiabatic saturation temperature of the gas with an ESP downstream of the spray dryer	Dry injection systems with baghouses remove 99+% of entrained product solids and fly ash ESP's demonstrate 99+% removal also, but SO_2 removal is much lower than in baghouses Also the increased inlet-grain loading will affect ESP sizing	Combustion of the coal/limestone fuel mixture will result in increased particulate loading
Special problems or advantages	Spray drying results in a dry easy to handle waste product When sodium alkalis are used, however, the products are quite water soluble and create disposal problems Water and energy requirements are less than for conventional "wet" lime/limestone systems High-sulfur coal applications may be limited, but are being investigated further	The dry product resulting is very water soluble, and leachability and stability problems are likely to occur in disposing the waste solids The use of relatively inexpensive reagent (nahcolite) and minimal equipment requirements make dry injection economically attractive The two major drawbacks are the availability of nahcolite in amounts required for commercial applications and the waste disposal problem	The additional costs of preparing the coal/limestone fuel and removing greater amounts of ash are significantly less than conventional wet scrubbing system costs However, these technologies have only been applied on small-scale industrial-type boiler systems
Development status	Spray drying is currently the only commercially applied dry FGD technology; three utility systems (400-500 MW each) are being constructed (startup in 1981, 82, and 83), and two industrial systems were scheduled to start up in late 1979 Several other companies are conducting extensive R&E programs toward a commercial system	Although dry injection has been shown to be technically feasible, commercial application is at a standstill because of uncertaint sorbent availability	Considerable work remains to develop the technologies for commercial scale applications, although industrial commercial applications look promising. EPA is currently funding continued pilot plant testing on industrial boilers, and more complete test work on low-NO_x burners has been proposed and is under review by the EPA.

[a] Utilization and removal figures are very site-specific and the given values should only be taken as a general indication of system performance. Removal and reagent utilizations may be lower or higher depending on system design, SO_2 inlet concentration, stoichiometric ratio, flue gas inlet temperature, temperature drop over the spray dryer, and fly ash alkalinity

reduced. It is estimated that dry removal units need only 25 to 50 percent of the energy that wet scrubbers require.[309] Finally, dry systems consume much less water than wet systems and thus are particularly attractive in western areas of the United States where water supplies are limited.

Several disadvantages have been put forth for dry scrubbing systems; among them are higher priced absorbents, applicability primarily to low sulfur coal, and that there are no commercially proven systems. It is true that the absorbents currently in use or planned employ dry lime scrubbing, with the exception of one regenerable Aqueous Carbonate system, rather than the less expensive limestone used successfully in many wet scrubbing systems.[310,311] Additionally, other more expensive absorbents, such as sodium carbonate, have been tested for use. Most of the dry systems either in design or under construction are for low sulfur (less than 1 percent sulfur) coal;[311,312] however, one industrial unit which is on stream reports 85 percent SO_2 removal when firing a 3 percent sulfur coal.[313] Therefore, dry systems may well be applicable to higher sulfur coals, but this will be shown only by more operating experience and research. The first commercial units, two identical systems, have begun operation,[313,314] and the first utility dry system is scheduled to begin operation in 1980.[315] More utility systems are scheduled on stream thereafter.

Process descriptions--[316]Dry systems can be regenerable, such as the Aqueous Carbonate Process, or nonregenerable, such as the lime systems.

In spray dryer-based systems, the first of the major types of dry FGD systems, flue gas at air preheater outlet temperatures [generally 135° to 204°C (275° to 400°F)] is contacted with a solution or slurry of alkaline material in a vessel of 5 to 10 seconds residence time. The flue gas is adiabatically humidified to within 28°C (50°F) of its saturation temperature by the water evaporated from the solution or slurry. As the slurry or solution is evaporated, liquid phase salts are precipitated and the remaining solids are dried to generally less than one percent free moisture. These solids, along with fly ash, are entrained in the flue gas and carried out of the dryer to a particulate collection device. Reaction between the alkaline material and flue gas SO_2 proceeds both during and following the drying process. The mechanisms of the SO_2 removal reactions are not well understood, so it has not been determined whether SO_2 removal occurs predominantly in the liquid phase, by absorption into the finely atomized droplets being dried, or by reaction between gas phase SO_2 and the slightly moist spray dried solids. The chemical reactions are identical to those described under corresponding wet scrubbing processes (e.g., lime, sodium carbonate, etc.).

Sodium carbonate solutions and lime slurries are common sorbents. A sodium carbonate solution will generally achieve a higher level of SO_2 removal than a lime slurry at similar conditions of inlet and outlet flue gas temperatures, SO_2 level, sorbent stoichiometry, etc. Lime, however, has become the sorbent of choice in many circumstances because of the cost advantage it enjoys over sodium carbonate and because the reaction products are not as water soluble. Through the use of performance enhancing process modifications, such as sorbent recycle and hot or warm gas bypass, lime sorbent has been demonstrated at the pilot scale to achieve high levels of removal (85 percent and greater) at sorbent utilization near 100 percent.

Using a spray dryer for a flue gas contactor involves adiabatically humidifying the flue gas to within some approach to saturation. With set conditions for inlet flue gas temperature and humidity and for a specified approach to saturation temperature, the amount of water which can be evaporated into this flue gas is set by heat balance considerations. Liquid to gas ratios are generally in the range of 0.03 to 0.04 liter/m^3 (0.2 to 0.3 gal/1000 ft^3). The sorbent stoichiometry is varied by raising or lowering the concentration of a solution or weight percent solids of a slurry containing this set amount of water. While holding other parameters such as temperature constant, the obvious way to increase SO_2 removal is to increase sorbent stoichiometry. However, as sorbent stoichiometry is increased to raise the level of SO_2 removal, two limiting factors are approached:

1) Sorbent utilization decreases, raising sorbent and disposal costs on the basis of SO_2 removed.

2) An upper limit is reached on the solubility of the sorbent in the solution, or on the weight percent of sorbent solids in a slurry.

There are at least two methods of circumventing these limitations. One method is to initiate sorbent recycle, either from solids which settle in the spray dryer or from material collected in the particulate collection device. This has the advantage of increasing the sorbent utilization; additionally, it can increase the opportunity for utilization of any alkalinity in the fly ash.

The second method of avoiding the above limitations on SO_2 removal is to operate the spray dryer at a lower outlet temperature; that is, a closer approach to saturation. Operating the spray dryer outlet at a closer approach to saturation has the effect of both increasing the residence time of the liquid droplets and increasing the residual moisture level in the dried solids. As the approach to saturation is narrowed, SO_2 removal rates and sorbent utilization generally increase rapidly. Since the mechanisms for SO_2 removal do not appear to be well understood, it is not obvious whether it is the increase in liquid phase (droplet) resident time, the increase in residual moisture in the solids, or both which account for the increased removal.

Unfortunately the approach to saturation at the spray dryer outlet is set by either the requirement for a margin of safety to avoid condensation in downstream equipment or restrictions on stack temperatures. The spray dryer outlet can be operated at temperatures lower than these restrictions would seem to allow if some warm or hot gas is bypassed around the spray dryer and used to reheat the dryer outlet. Warm gas (downstream of the boiler air heater) can be used at no energy penalty, but the amount of untreated gas involved in reheating begins to limit overall SO_2 removal efficiencies. Figure 4.2-39, a general flow diagram of a spray dryer based system, illustrates these two "reheat" options.

The spray dryer design can be affected by the choice of particulate collection device. Bag collectors have an inherent advantage in that unreacted alkalinity in the collected waste on the bag surface can react with remaining SO_2 in the flue gas. Some process developers have reported SO_2 removal on bag surfaces on the order of 10 percent. A disadvantage of using a bag collector is that since the fabric is somewhat sensitive to wetting, a margin above saturation temperature [on the order of 14° to 19°C (25° to 35°F)] must be maintained for bag protection. Electrostatic precipitator (ESP) collectors have not been demonstrated to achieve significant SO_2 removal. However, some vendors claim that the ESP is less sensitive to

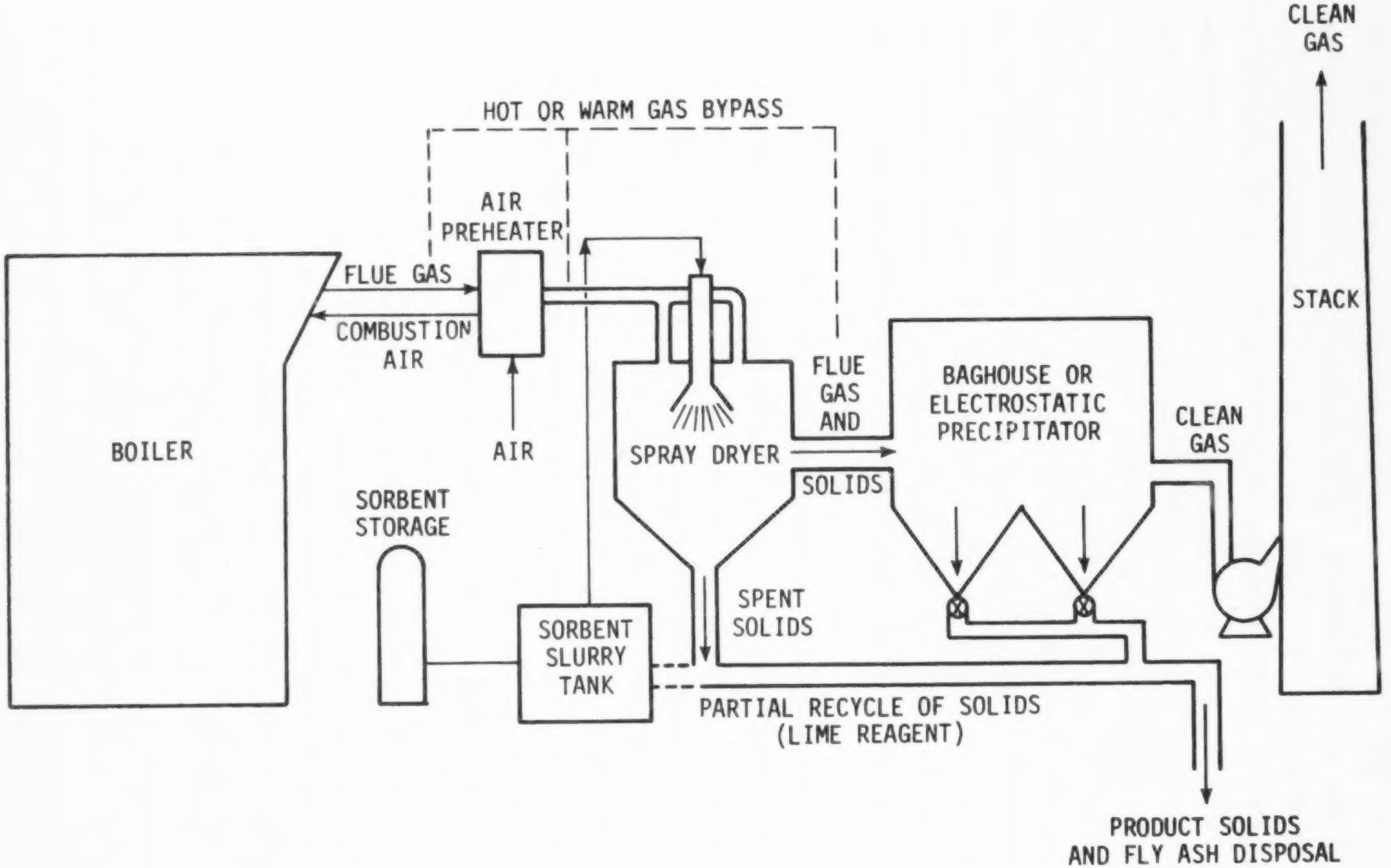

CLEAN GAS
HOT OR WARM GAS BYPASS
AIR PREHEATER
FLUE GAS
COMBUSTION AIR
BOILER
AIR
SORBENT STORAGE
SORBENT SLURRY TANK
SPRAY DRYER
FLUE GAS AND
SOLIDS
SPENT SOLIDS
BAGHOUSE OR ELECTROSTATIC PRECIPITATOR
CLEAN GAS
STACK
PARTIAL RECYCLE OF SOLIDS (LIME REAGENT)
PRODUCT SOLIDS AND FLY ASH DISPOSAL

Figure 4.2-39. Typical Spray Dryer Particulate Collection Flow Diagram.[317]

condensation and hence can be operated closer to saturation [less than a 14°C (25°F) approach] with the associated increase in spray dryer performance.

The choice between sorbent types, use of recycle, use of warm or hot gas bypass, and types of particulate collection device tends to be site specific. Vendor and customer preferences, system performance requirements, and site specific economic factors tend to dictate the system design for each individual application.

The second major type of dry FGD system, the dry injection process, generally involves pneumatically introducing a dry, powdery alkaline material into a flue gas stream with subsequent particulate collection. A generalized flow diagram of this process is shown in Figure 4.2-40. The injection point has been varied from the boiler furnace area all the way to the flue gas entrance to an ESP or bag collector. Most dry injection schemes use a sodium-based sorbent. Lime has been tested but has had little success. Many dry injection programs have used nahcolite as a sorbent. Nahcolite is a naturally occurring mineral, associated with western oil shale reserves, and is about 70 percent sodium bicarbonate. Sodium bicarbonate appears to be more reactive than sodium carbonate because it loses both two moles of CO_2 and one of water in reaction, while sodium carbonate loses only one mole of CO_2 in reaction with SO_2. The following overall reactions illustrate this point:

$$2\ NaHCO_3 + SO_2 \rightarrow Na_2SO_3 + 2CO_2 + H_2O$$

$$Na_2CO_3 + SO_2 \rightarrow Na_2 + CO_2$$

Unfortunately, the availability of raw nahcolite in commercial quantities in the near future is questionable due to the substantial investment necessary before commercial scale mining can begin. Since the favorable economics of dry injection are based to some extent on the use of inexpensive sorbents, the use of commercially refined sodium bicarbonate is prohibitively expensive. Recent research has been aimed at studying the use of raw trona ore, which is currently mined in large quantities both in the Green River, Wyoming area and the Owens Lake, California area. The mineral trona contains one mole of sodium carbonate, one mole of sodium bicarbonate and two waters of hydration ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$). Trona has the potential for

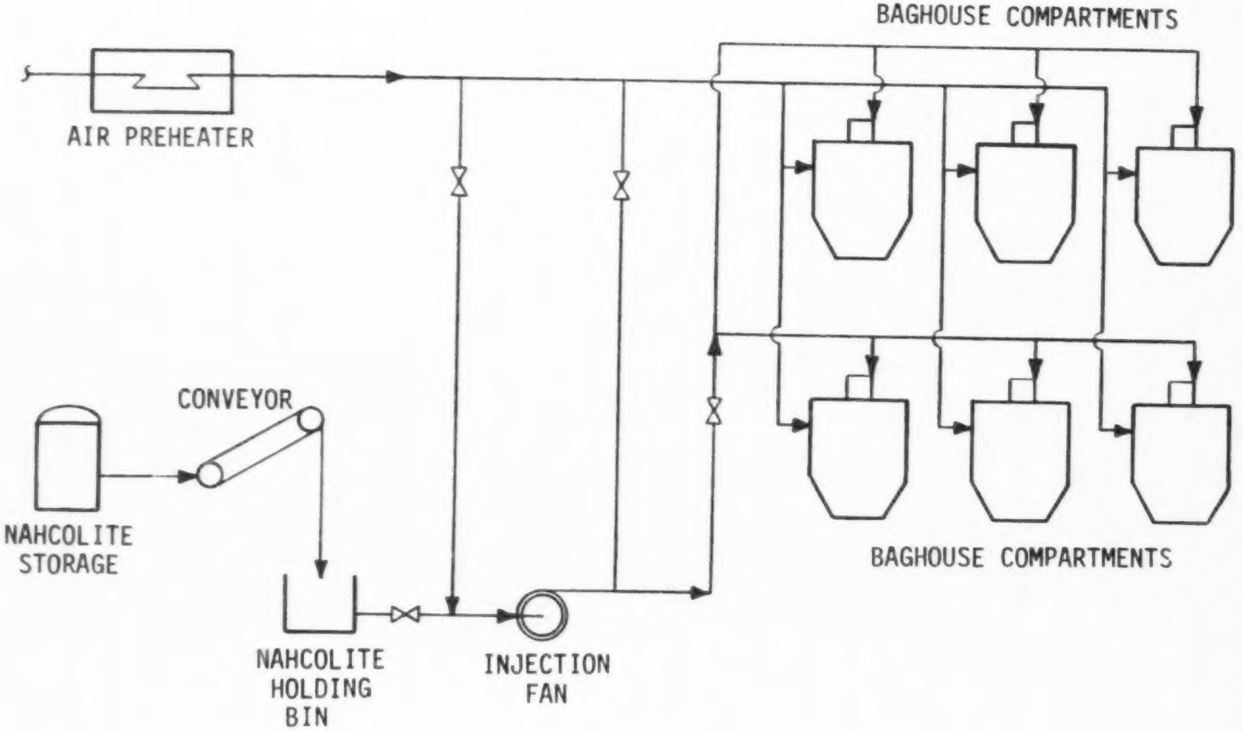

BAGHOUSE COMPARTMENTS
AIR PREHEATER
CONVEYOR
NAHCOLITE STORAGE
NAHCOLITE HOLDING BIN
INJECTION FAN
BAGHOUSE COMPARTMENTS

Figure 4.2-40. Nahcolite dry injection flow diagram.[318]

providing a good compromise between reactivity, cost, and availability for use in dry injection schemes.

An unresolved problem with this technology is disposal of the sodium-based waste materials in an environmentally acceptable manner. Sodium waste materials are highly soluble and can result in contamination of aqueous streams. Disposal of sodium compounds is an area requiring further investigation.

Both baghouse and ESP collection devices have been tested with dry injection processes. However, the effect of the reaction between unspent sorbent on collected bag surfaces and SO_2 remaining in the flue gas favors the bag collector. Since a major portion of the SO_2 removal reaction appears to take place on the bag surface, various methods of feeding have been tested.

Three types of feeding are:

1) After the bag is cleaned, sorbent is added to the bag surface only as it is entrained with the flue gas from a continuous upstream injection point. This method is called continuous feeding.

2) After bag cleaning, all sorbent is added to the bag as a precoat before flue gas flow is resumed. This is considered batch feeding.

3) A compromise between types 1 and 2, after bag cleaning some sorbent is added initially as a precoat and the remainder is added continuously through the bag cycle at some upstream injection point. This method of feeding is called "semi-batch" feeding.

Also varied in dry injection programs are sorbent stoichiometry, sorbent particle size, point and temperature of injection, baghouse air-to-cloth ratio, and bag cleaning frequency.

The current research on the combustion of a coal/limestone fuel mixture, the third major dry FGD system option, has taken two forms:

1) Combustion of a coal/limestone pellet in an industrial spreader-stoker boiler.

2) Combustion of a pulverized coal/limestone mixture in a low-NO_x burner system.

Preliminary results of test work on both processes have indicated that up to 80 percent of the available sulfur in the fuel can be retained by the limestone. The ratio of calcium to sulfur in the coal/limestone fuel mixture is important in determining how much sulfur is retained.

A spreader-stoker boiler has been used in testing the combustion and sulfur retention characteristics of the coal/limestone pellet. A Ca:S mole ratio of 7:1 has been used so far, but further work with a 3:1 Ca:S pellet is planned. The emissions generated are dependent upon boiler-system design, coal properties and combustion operating parameters. The inherent staged combustion of the stoker-fired boiler (accomplished by supplying the total combustion air as primary air through the grates and secondary air through over-fire jets above the bed) results in lower NO_x emissions relative to conventional pulverized coal-fired boilers.

The two-staged combustion concept was employed by Babcock & Wilcox (B&W) to design an advanced low-NO_x burner system. EPA has funded test work to develop a concept of firing a coal/limestone fuel mixture in B&W low-NO_x burners to reduce SO_2 emissions. Tests conducted on a 12.7 GJ (12×10^6 Btu)/h scale by the Energy and Environmental Research Corporation (EERC) with a Utah low sulfur coal have demonstrated 88 percent SO_2 removal with a 3:1 Ca:S mole ratio. This high SO_2 removal has been attributed to the lower flame temperature found in the low-NO_x burner which may help maintain limestone reactivity. The EERC has reported that SO_2 removal increased substantially when the reagent was passed through the pulverizer with the coal.

Further research on a larger scale for both systems is needed to determine the effects of combustion of a coal/limestone fuel mixture on boiler operation and maintenance. Collection of the increased ash loading and investigation of the properties and disposal of the waste products must also be studied.

Technological development--Many studies, which are discussed later, have been made of dry systems that use a fabric filter alone. The technology of this process, however, is not advancing rapidly. No full-scale applications of dry removal with only a fabric filter are currently planned; however, EPRI will support a 25-MW demonstration of this concept at the Cameo Station in Colorado. Perhaps the most promising sorbent for this process is nahcolite, which is found in tremendous reserves in the Piceance Creek Basin of Colorado. The three companies that hold leases in the area are unwilling to mine nahcolite on a commercial scale until they receive substantial commitments from customers.[319]

Several factors affect SO_2 removal by dry systems. For example, removal efficiency generally increases as flue gas temperature and residence time increase,[320] but this depends to some extent upon the absorbent. Removal efficiency also improves with a high stoichiometric ratio of sorbent to SO_2. Sodium-based dry sorbents display significantly higher reactivity than calcium- or magnesium-based sorbents.[320]

The SO_2 removal efficiency of fabric filter systems has improved since early tests. Pilot-scale runs with only a sorbent-coated fabric filter at the Edwardsport Station of Public Service of Indiana from 1967 to 1977 resulted in SO_2 removal efficiencies from 13 to 72 percent with alkali utilizations of 22 to 93 percent; high removal efficiencies, however, were possible only at unacceptably low alkali utilizations.[321] The only sorbents found consistently effective were Na_2CO_3 and $NaHCO_3$. In mid-1974 tests at the Nucla Station of Colorado-Ute Electric Association, the highest SO_2 removal efficiency with nahcolite as the sorbent was 70 percent with 56 percent alkali utilization when a 0.8 percent sulfur coal was burned.[322] In late 1974 tests at the Hoot Lake Station of Otter Tail Power Company, the average SO_2 removal efficiency of 94 percent was observed immediately after precoating.[323] In late 1976 at the Leland Olds Station of Basin Electric, the SO_2 removal efficiency with nahcolite was at first 83 percent with 77 percent alkali utilization and later 90 percent with 60 percent alkali utilization.[324]

Two-stage dry systems can achieve high SO_2 removal efficiencies, as shown by tests of the Aqueous Carbonate Process, a regenerable process that Atomics International has developed, with a solution of sodium carbonate as the sorbent. All the removal efficiencies observed during 26 laboratory tests in May 1973 were 90 percent or more. During 40 similar tests in June 1973, the removal efficiencies ranged from 92 to 99 percent, and more recent tests have yielded comparable results.[325]

Basin Electric anticipates that the SO_2 removal efficiencies of its two-stage dry removal systems will be moderate to high. The spray dryer using a lime and fabric filter system at Antelope Valley Unit 1 is designed to operate at 62 percent SO_2 removal efficiency for lignite containing 0.68

percent sulfur and 78 percent efficiency for lignite containing 1.22 percent sulfur.[326] The spray dryer and ESP at Laramie River Unit 3 are designed to operate at 85 percent SO_2 removal efficiency for 0.54 percent sulfur coal and 90 percent efficiency for 0.81 percent sulfur coal.[327] The lime feed rate of the Antelope Valley Unit 1 system will be essentially at a stoichiometric ratio of 1 because of the utilization of available alkalinity in the fly ash.[326] The estimated annual consumption of lime by the Laramie River Unit 3 system indicates that Basin Electric also expects the lime feed rate for that system to be essentially at a stoichiometric ratio of 1.[328]

Moderate SO_2 removal efficiencies are also expected at two lime-based, two-stage systems at industrial facilities. The design removal efficiency of the spray dryer and fabric filter at the Strathmore Paper Company in Woronoco, Massachusetts, is 75 percent when coal with a sulfur content of from 0.75 to 3.0 percent is fired.[329] This is a retrofit installation on an industrial boiler with a gas flow capacity equivalent to an 11-MW utility boiler.[329] At the Celanese Fibers Company plant in Cumberland, Maryland, the SO_2 removal efficiency of the planned spray dryer and fabric filter was anticipated to be 85 percent for coal containing 1.0 to 2.0 percent sulfur;[330] however, compliance tests showed 85 percent removal at 3.0 percent sulfur coal.[313]

A 2-year test program of the Atomics International Aqueous Carbonate Process, a regenerable dry FGD process, is scheduled to begin in 1982 at the 100-MW Huntley Station of Niagra Mohawk in Tonawanda, New York; this process regenerates spent sodium carbonate and produces elemental sulfur with coal as the reductant.[331]

Compilations of the status of dry sorbents and fabric filter filtration for FGD have recently been published; these compilations address many of the concerns, problems, and solutions for these systems.[332],[333]

Costs--The costs of dry removal systems are very site-specific. The type of fuel and sorbent, the fuel sulfur content, the flue gas volume treated, the desired control efficiency, the plant location, and other variables greatly affect costs. Despite the wide variations such variables can cause, sufficient information is available to allow rough cost estimates.

The key features of five dry systems including estimated capital and operating costs are given in Table 4.2-41.[334]

The costs of two-stage systems have received much attention. Recent studies indicate that the capital cost of a two-stage system depends greatly on the flue gas flow rate. The mid-1979 capital cost of such a system is estimated to be about $87/kW for a 440-MW utility plant and $65/kW for a 600-MW plant with about the same flue gas flow rate.[335] Thus, the total installed capital cost is roughly the same for the plants. In general, the mid-1979 capital cost of a two-stage dry system designed to control both SO_2 and particulate emissions ranges from $55/kW to $98/kW.[335]

The annual operating costs of a two-stage dry system include the costs of the reactant, operating labor, steam, electricity, water, chemical analyses, maintenance, waste disposal, and items characteristic to a particular system. With a two-stage system, a utility plant uses between 1.25 and 1.75 kg of lime per kg of SO_2 removed (1.25 to 1.75 lb of lime per lb of SO_2 removed).[335] The cost of operating labor depends on the size of the system and the degree of automation; two persons per shift should be adequate.[335] A two-stage dry system may use steam in some climates for heat tracing of feed tanks and lines. The electrical costs cover mainly the power to drive the atomizers and the incremental power needed by the fans to overcome the system pressure drop. The dry system uses about 1.14 liters (0.3 gal) of water to treat 28.3 m^3 (1000 ft^3) per minute of flue gas. Because most of the water can come from the ash pond, cooling tower blowdown, or other plant or boiler waste streams, the cost of water may be small. Chemical analysis requirements are also low because of the simplicity of the process.[335] Maintenance costs can vary widely according to preventive maintenance schedules and crews; as of mid-1979, however, annual maintenance is estimated to cost about $1.09 for every installed kilowatt of capacity.[335] Waste disposal costs are those incurred in disposing of the mixture of fly ash, dry product, and unused reactant; this mixture contains less than 0.2 percent water by weight and thus costs much less to transport to a disposal site than sludge from a wet scrubber.[335]

One source estimates a total annual operating cost of roughly $11,400,000 and an annualized cost of 3.27 mills/kWh for a two-stage dry

TABLE 4.2-41. SUMMARY OF KEY FEATURES OF COMMERCIAL SPRAY DRYING SYSTEMS[334]

System	Generating capacity	System description	Sorbent	Coal	SO_2 removal guarantee	Sorbent utilization guarantee	Estimated capital cost	Estimated operating costs
Rockwell/Wheelabrator-Frye Otter Tail Power Co.'s Coyote Station, Unit 1, Beulah, ND Startup date June, 1981	410 MW (1,890,000 acfm)	Four Bowen 46-ft-diameter spray towers in parallel, each equipped with three centrifugal atomizers, combined with a multicompartment Wheelabrator-Frye fabric filter with dacron bags, (reverse-air, shaker cleaned). Process known as Open-Loop (no sorbent regeneration)	Soda ash	North Dakota lignite. Average S, 0.78% 7050 Btu/lb, HHV 7% ash	70% for all fuels	60%	$32,000,000 ($78/kW)	$56,580,000/yr, $2.5 mils/kWh, Does not include waste disposal cost
Joy/Niro Basin Electric's Antelope Valley Station, Unit 1, Beulah, ND Startup date April 1982	440 MW (2,200,000 acfm)	Five 46-ft-diameter spray modules (four with ducted spare) in parallel, each equipped with a single high horsepower rotary atomizer, combined with a Joy (Western Precipitation) multicompartment fabric filter with Teflon coated fiberglass bags (reverse-air cleaning). The system also includes a partial recycle of product solids/fly ash mixture	Lime	North Dakota lignite Average S, 0.78% Maximum S, 1.22%	62% for avg. S coal 78% for max. S coal	Not reported	$49,665,100 ($113/kW)	$2,278,834/yr, 0.8 mils/kWh, sorbent cost (lime), $1,102,500 ($60/ton basis) Does not include waste disposal cost
Babcock and Wilcox Basin Electric's Laramie River Station, Unit 3, Wheatland, Wyoming Startup date Late 1979	600 MW (2,810,000 acfm)	Four reactors (one spare) operated in parallel, each followed by an ESP. Each reactor is equipped with 12 "Y" jet nozzles which are dual-fluid atomizers that use steam as the atomizing fluid. ESP's, B&W Rothemule	Lime	Wyoming sub-bituminous Average S, 0.54% Maximum S, 0.81% 8140 Btu/lb, HHV 8% ash	85% for avg. S coal 90% for max. S coal	Maximum stoichiometric ratio of about 1.12	$49,807,000 ($83 $/kW)	$2,571,000/yr, 0.7 mils/kWh, sorbent cost (lime), $1,396,570 ($60/ton basis). Does not include waste disposal cost
Mikropul, Strathmore Paper Co., Woronoco, Mass Startup date Late 1979	Industrial Boiler (40,000 acfm)	Spray dry followed by Mikro-Pulseair pulsejet baghouse	Lime	2 to 2.5% S	75% on 3% S coal	Maximum stoichiometric ratio of 2.75	$ 1,400,000	$162,000/yr, 2.3 mils/kWh
Rockwell/Wheelabrator-Frye, Celanese Corporation Cumberland, Maryland Startup Date Late 1979	Industrial Boiler (67,000 acfm)	One 25-ft-diameter spray tower followed up by a four-compartment baghouse. Dry waste product will be mixed with lime and trucked to dumping area	Lime	1 to 2% S	85%	Not reported	$ 1,250,000	Not available

removal system with lime sorbent at a 500-MW utility plant.[335] (These values have been adjusted from May 1978 to mid-1979.) The plant is assumed to operate 7000 h/yr, to fire coal containing 2 percent sulfur and 10 percent ash, and to achieve an SO_2 removal efficiency of 80 percent. About 60 percent of the annualized cost estimated for a new system covers direct operating expenses, and 40 percent covers the capital charge on the total investment, assumed to be about $76/kW as of mid-1979.[335]

Basin Electric Power Cooperative plans to use the two-stage dry removal process at two lignite-fired units: the 440-MW Unit 1 of the Antelope Valley Station near Beulah, North Dakota, and the 600-MW Unit 3 of the Laramie River Station near Wheatland, Wyoming. Table 4.2-42 presents the total costs of dry removal at these units for an estimated life of 35 years.[336] The FGD system at Antelope Valley will consist of a spray dryer with a rotary atomizer and a fabric filter. The system at Laramie River will include a spray dryer with a "Y-jet" nozzle and an ESP. Lime will be the sorbent for both systems; the estimated annual lime consumption rates are 16,350 Mg (18,000 tons) at Antelope Valley and 19,000 Mg (20,920 tons) at Laramie River.[336] The annual power requirements will be approximately 5726 kW for Antelope Valley and 2451 kW for Laramie River. The estimated manpower for each system is six operators and seven maintenance persons. At Laramie River, the system will have to overcome a pressure drop of 1.6 kPa (6.5 in. H_2O) between the air heater outlet and stack inlet. The SO_2 removal efficiencies are expected to range from 62 to 78 percent at Antelope Valley and from 85 to 90 percent at Laramie River. According to Basin Electric, the total savings of two-stage dry removal over wet limestone scrubbing amount to a 36 percent cost reduction at Antelope Valley and 17 percent at Laramie River.[336]

Energy and environmental impacts--Dry removal requires less energy than wet scrubbing because normally the temperature of the flue gas is not greatly lowered and because saturation is not reached. Energy-consumptive reheat is thus minimized or eliminated.[337] According to Basin Electric, a dry system needs only 25 to 50 percent of the energy required by a wet system.[309]

TABLE 4.2-42. ESTIMATED COSTS OF TWO-STAGE DRY REMOVAL
FOR 35 YEARS[336]
(thousands of mid-1979 dollars)[a]

	Antelope Valley Unit 1	Laramie River Unit 3
Capital investment	41,450	41,569
Lime	32,205	40,795
Electricity	6,232	4,011
Manpower	13,291	13,291
Replacement parts	14,606	13,145
Pressure drop		3,859
Total	107,784	116,670
Average annual cost	3,080	3,333

[a] The Basin Electric estimates were given for December 31, 1981. These estimates were backdated to July 1, 1979, on the assumption that the inflation rate for each item will be 7.5 percent from mid-1979 to the end of 1981.

Waste from a sodium-based system can pose environmental problems. Because the portion of the waste that is soluble ranges from 50 to 60 percent,[338] substantial leaching may occur unless the disposal site is lined.

Waste from a calcium-based system is moderately cementitious and impermeable. The solubility of such waste has been measured at 3 to 7 percent.[338] Basin Electric plans landfill disposal of the calcium sulfate and sulfite waste from its two-stage dry removal systems. Although significant leaching appears unlikely, other problems may occur, such as weathering, erosion, fugitive dust, and structural instability.[338] Disposal procedures will be determined when the dry product becomes available. Currently, the disposal of waste from a calcium-based system appears no more dangerous or difficult than the disposal of fly ash.[338] Disposal of the used dry absorbent and fly ash at the mines where the absorbent is obtained is being investigated.

4.2.4 Combined Coal Cleaning/FGD

The control of these SO_2 emissions can be partially or totally achieved with current technology through coal cleaning, flue gas desulfurization (FGD), or the combined use of cleaned coal with partial FGD. The subject of coal cleaning is addressed in Section 4.2.2.1, and nine FGD processes are discussed in Section 4.2.3. The combination of these technologies in the achievement of SO_2 control will be discussed in this section.

Although coal washing cannot always eliminate the need for flue gas scrubbing, the required SO_2 removal can be significantly reduced. For a 520 ng/J (1.2 $lb/10^6$ Btu) SO_2 emission limit with a 3.5 percent sulfur, 27,900 J/g (12,000 Btu/lb) coal being fired, the required SO_2 removal could be reduced from 80 percent to 60 percent.[339] Similarly for a 260 ng/J (0.6 $lb/10^6$ Btu) case with the same coal being fired, the required SO_2 removal could be reduced from 90 to 81 percent. One impact of the reduced SO_2 removal requirement for an FGD system is that a partial bypass of the untreated flue gas may be possible to provide the required reheat for the cleaned flue gas. A second impact is to reduce the stringent, continuous SO_2 removal requirement that may be required of an FGD unit. Another impact is to improve the operation of the boiler because of the cleaner fuel being fired, which should also reduce the maintenance costs related to boiler operation, as previously noted.

A major consideration that can affect FGD system design is that the use of cleaned coal can significantly reduce the volume of sludge generated. In a study based on the old NSPS for a utility boiler emitting 520 ng SO_2/J (1.2 lb $SO_2/10^6$ Btu) and based on a 3.5 percent sulfur coal with a heating value of 27,900 J/g (12,000 Btu/lb), a 500-MW generating unit, and 40 percent sulfur removal by physical coal cleaning, the annual volume of sludge generated is 149,000 m^3 (121 acre-feet) for a lime-based FGD system and 155,000 m^3 (126 acre-feet) for a limestone-based FGD system. Without coal cleaning, the annual sludge volume generated is 286,000 m^3 (232 acre-feet) for a lime-based system and 299,000 m^3 (242 acre-feet) for a limestone-based system. This represents a 48 percent reduction in the sludge that must be handled, treated, and stored or disposed of. If ash disposal is included, the total solids that must be handled reflects a 44 percent reduction if coal cleaning were used for lime and limestone FGD systems.[340]

4.2.4.1 Combined Coal Cleaning and FGD Costs--

Sulfur dioxide emission limitations when firing high-sulfur coal would require additional SO_2 removal by an FGD system after coal cleaning. In one study, several cases were examined to evaluate the economic benefits obtainable by the use of coal cleaning in combination with FGD versus FGD alone. A single plant scenario is examined in which a single boiler is served by a coal cleaning plant and a lime or limestone FGD system is installed to meet the regulation level. In the first case, a 500-MW unit burning 3.5 percent sulfur coal and required to meet a 520 ng SO_2/J (1.2 lb $SO_2/10^6$ Btu) regulation was considered. Considered in the second case were boilers of 25, 200, and 500 MW burning 7.0 percent sulfur coal and required to meet a 215 ng/J (0.5 lb/10^6 Btu) regulation level. Table 4.2-43 presents the washability data for the two coals.[341]

Case 1 involves 40 percent removal of sulfur by coal washing of a 3.5 percent sulfur coal. Conventional coal preparation can be applied to many U.S. coals to achieve a 40 percent reduction in sulfur. In this situation, the model coal selected is an Illinois coal with a raw coal sulfur content of 3.48 percent. The U.S. Bureau of Mines washability data indicate that

TABLE 4.2-43. WASHABILITY DATA FOR HIGH SULFUR COALS[341]

Washing gravity	Weight recovery, %	Heating value recovery, %	Heating value, J/g (Btu/lb)	Sulfur, %	Ash, %
1.3	21.9	26.3	32,900 (14,100)	1.32	2.6
1.3 x 1.4	62.5	73.1	32,000 (13,700)	1.66	5.3
1.4 x 1.6	82.4	93.4	31,000 (13,300)	1.97	8.2
1.6 x 1.9	85.9	96.3	30,600 (13,100)	2.09	9.2
Raw coal	100.0	100.0	28,000 (12,100)	3.48	14.0
1.3	52.2	59.8	32,700 (14,000)	2.13	1.9
1.3 x 1.4	74.4	81.1	32,400 (13,900)	2.54	2.7
1.4 x 1.6	83.3	93.1	32,000 (13,700)	2.90	4.2
Raw coal	100.0	100.0	28,000 (12,000)	6.40	14.0

cleaning at 1.8 specific gravity (s.g.) will reduce the sulfur content by about 50 percent with a Btu yield of 93.4 percent; the data also indicate a 45 percent reduction in sulfur at 1.9 s.g. with a 96.3 percent Btu yield. Assuming that the higher cleaning gravity is used and that a grass roots cleaning plant is built, the capital costs of cleaning should be in the range of \$8,650 to \$26,000 per ton per hour of raw coal processed. For a state of the art cleaning plant, operating 4000 hours/year and processing approximately 1.45 Tg (1,600,000 tons) per year of raw coal, the capital investment is estimated to be approximately \$3,030,000 to \$7,180,000. Since the size of this cleaning plant is small, the cost is estimated on the high side of the range at \$6,700,000. Operating costs are estimated to be 2.47 to 3.72 mills/kWh. The additional coal required, because of heat value lost with the coal cleaning refuse, is estimated to be about 90.7 Gg (100,000 tons) annually. At an assumed cost of \$1.14/GJ (\$1.20/10^6 Btu), the additional costs for coal would be \$2,800,000 (0.98 mills/kWh).[342]

Case 2 was evaluated in exactly the same manner as Case 1 using washability data for the 7.0 percent sulfur coal. Costs do not differ appreciably from those obtained for Case 1.

For a 520 ng SO_2/J (1.2 lb SO_2/10^6 Btu) regulation case, combined coal cleaning and lime or limestone FGD are more expensive than either lime or limestone FGD alone. Capital costs are about 1.5 percent higher, while annual costs are about 36 percent higher.[342] Possible improved boiler operation, reduced boiler maintenance, and reduced energy requirement by utilizing flue gas bypass for cleaned flue gas reheat are not considered in the annual costs.

It appears that the major benefit from the use of combined coal cleaning and FGD is in cases where FGD alone cannot attain the level of control required.

One source states that, in some cases, under current state and Federal standards, the SO_2 control costs of using FGD in combination with physical coal cleaning may be lower than those for using FGD alone.[343]

4.2.5 Combustion Process Modifications

Any improvement in the efficiency of a combustion process that reduces the fuel requirement will reduce both fuel costs and pollutant emissions.

With conventional combustion systems, regular maintenance and proper operation will help ensure peak operating efficiency. Some advanced combustion processes offer potential for further reduction in fuel requirements over conventional systems and some also may reduce SO_x emissions.

4.2.5.1 Conventional Combustion Systems--

Inefficient operation of the conventional combustion systems, whether fired with coal, oil, or natural gas, can cause an increase in pollutant emissions through increased fuel use or incomplete combustion. One cause of inefficiency is an improper air/fuel ratio. Operation with insufficient air (fuel-rich) can result in unburned fuel, whereas operation with too much air reduces efficiency by allowing the air to absorb heat unnecessarily and carry it out the stack. Combustors should be checked periodically to ensure the proper air/fuel ratio for optimum efficiency.

Incorporation of economizers and air preheaters is common in new installations. An economizer recovers heat and raises the feedwater temperature. An air preheater can also increase efficiency by reducing the stack temperature and improving combustion conditions. Both types of equipment can effect reduction of pollutant emissions by enhancing fuel utilization. Retrofitting of such equipment at existing installations, however, could be cost-prohibitive.

4.2.5.2 Fluidized Bed Combustion--

The fluidized bed process has been known since the 19th century and has been used extensively in the petroleum industry. Its relatively recent application to coal combustion offers several advantages over conventional combustion methods.

Because heat release and heat transfer are higher in fluidized beds of coal and air than in conventional furnaces, smaller (and perhaps less costly) units can be used for a given generating capacity. Fluidized bed combustion is being investigated at atmospheric and elevated pressures. Operation above atmospheric pressures offers higher combustion efficiency, greater unit capacity, and the potential for use of a combined-cycle system for even higher thermodynamic efficiency.

As an SO_x emission control technique, fluidized bed combustion appears to provide cleaner burning of high-sulfur coals. Limestone or dolomite added to the fluidized bed absorbs sulfur released during combustion to form sulfates. The temperature of the fluidized bed is high enough to calcine limestone or dolomite to lime but low enough that the sulfate will not dissociate. Research has shown that sulfur removal can be greater than 90 percent; the resultant waste is dry and therefore easier to handle than a slurry or sludge.

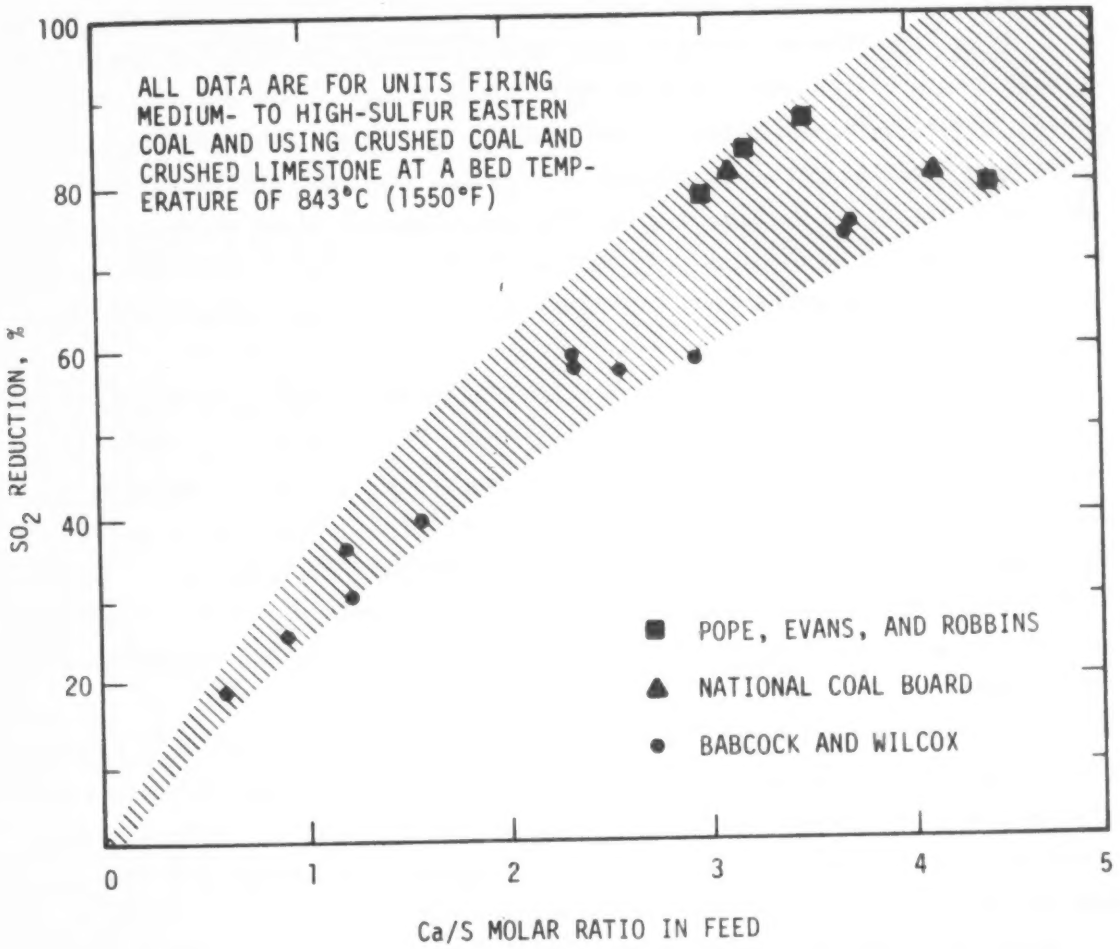
Most of the development work on fluidized bed combustion has been with small devices. It is not known whether data from this work can be directly extrapolated to large, commercial-scale units. Operation of some larger demonstration units being planned will provide additional data on several critical aspects of fluidized bed combustion.

Among the prime concerns in process development is the calcium/sulfur (Ca/S) ratio, which is the ratio of the limestone/dolomite (sorbent) required for each unit of sulfur removed. Ratios are reported to range from 2 to 4.5.[344,345] High rates of SO_2 reduction can require large quantities of sorbent and thus generate large quantities of waste. Methods being developed to improve sorbent utilization include low bed velocities, regeneration of spent sorbent, and use of additives to the sorbent. Figure 4.2-41 shows the relationship of Ca/S ratio to sulfur reduction.[345] Other developments are concerned with recycling of elutriated fines to improve efficiency, coal/sorbent feed systems, load response, bed dynamics and heat transfer, and natural circulation.

4.2.5.3 Advanced Combustion Systems--

An extension of atmospheric fluidized bed combustion (AFBC) is pressurized fluidized bed combustion (PFBC), in which combustion occurs at 6 to 16 times atmospheric pressure. Though not as highly developed as AFBC, PFBC appears to offer advantages.

Combined-cycle power generation is one of the advantageous features of PFBC. Utilizing the combustion gases in a gas turbine, as well as for steam generation, offers the potential of attaining 40 percent system efficiency versus 37 percent for AFBC.[346] Pressurized FBC also provides potential for smaller unit size and greater sorbent utilization. Development of gas



345

Figure 4.2-41. Once-through SO_2 reduction versus Ca/S molar ratio.

turbines suitable for coal-fired service is a primary impediment to commercial application of PFBC technology, which is not expected before 1985-1990.[347-348]

Magnetohydrodynamics (MHD) is a means of directly converting the energy of a high-temperature, ionized gas stream into electricity by passing it through a magnetic field. Extremely high gas temperatures and addition of a "seed" material are necessary for satisfactory gas conduction/ionization. Since the exhaust gases would be at a high temperature [1650°C (3000°F)], an MHD could serve as a topping cycle for conventional steam power generation with system efficiencies as high as 50 to 60 percent.[349-351] This would, however, require modification to the conventional system to make it compatible with MHD.

The high system efficiencies achievable by MHD will reduce fuel use and thus pollutant emissions. Researchers have found that a potassium seed material will combine with the SO_2 to form potassium sulfate (K_2SO_4), which can be removed by conventional pollution control devices as it solidifies upon gas cooling.[352] Studies are under way to develop methods of regenerating the potassium seed material while collecting the sulfur. There are indications that care must be taken to avoid extensive NO_x emissions from MHD systems.

The MHD is not expected to be available until the end of this century. The United States and the USSR are participating in a cooperative research program, but difficult technical problems still must be solved. Major problems include combustor performance, slag/seed separation and recovery, erosion, corrosion, and material requirements.[349,353]

Many other methods of increasing the efficiency of coal combustion have been studied and proposed. Advanced power cycles promise to reduce the amount of emissions per unit of useful power produced in addition to reducing fuel consumption. Although most of these methods are not yet economically feasible or developed far enough to permit widespread use, combined cycle gas turbines are currently being used to produce electrical power on a commercial basis. The desire to make these systems compatible with coal or synthetic coal-derived fuels complicates the problems. In addition, new combustors are being developed to reduce the NO_x emissions, which are generally greater than for a similar sized unit burning distillate fuel oil.

In addition to MHD, the primary advanced power cycle candidates for commercial use are open-cycle gas turbine combined cycles, closed-cycle power systems, and fuel cells.[354] The combined cycles utilize steam turbine and gas turbine technology together to increase efficiency. Use with coal firing presents materials problems (erosion, stress, temperature) requiring solutions. Methods must be found for cleaning the hot gases to maintain efficiency and prevent pollution and corrosion.

Closed-cycle power systems also utilize gas turbines but with an inert gas or liquid metal as the working fluid in lieu of combustion gases. High efficiency can be attained by operation at high temperatures with a steam-bottoming cycle. Again, materials problems preclude use of these systems before 1990.[355]

Fuel cells involve the electrochemical generation of electricity by combining hydrogen and oxygen or oxygen and a mixture of hydrogen and carbon monoxide. Coal-derived synthetic gas will fuel second-generation development units. Because combustion gases must be clean before entering the fuel cell, techniques for hot gas cleanup are needed.[356]

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SECTION 5

INDUSTRIAL PROCESSES

In this chapter, the largest process emitters of sulfur oxides are discussed. The method of presentation is a description of the process including the source or sources of sulfur oxide emissions from the process, the applicable or currently practiced sulfur oxide control technique(s), the capital and annual costs associated with the control system (presented in mid-1979 dollars), and a discussion of the energy and environmental impacts associated with the control system. The information reported here is a condensation of information reported in the open literature.

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5.1 NONFERROUS PRIMARY SMELTERS

5.1.1 Process Description and Emission Sources

This section examines the production of the five principal nonferrous metals: copper, lead, zinc, aluminum, and molybdenum. With the exception of aluminum, the ores of these metals contain sulfur as a principal constituent. An integral part of the processing operations is to separate the sulfur from the metals; this separation is usually accomplished by oxidation, which results in sulfur dioxide emissions.

5.1.1.1. Copper Smelters--

The production of copper begins with the processing of various copper ores, which contain a small percentage of copper sulfide, such as the following:[1]

- chalcocite - Cu_2S - 79.8 percent copper
- bornite - Cu_5FeS_4 - 63.3 percent copper
- tetrahedrite - $Cu_5Sb_2S_7$ - 57.5 percent copper
- chalcopyrite - $CuFeS_2$ - 34.5 percent copper

The percentage of copper in most ores mined is rarely above 1 percent, and therefore the ore is concentrated in almost all cases by flotation. Concentration ratios may range from 5 to 1 to 40 to 1.[1] Sulfide ores are mixtures of varying proportions of copper and iron sulfides mixed with acidic or basic gangue. The conversion of iron sulfides to iron oxides occurs preferentially to the conversion of copper sulfides to copper oxides.

As practiced in domestic plants, smelting consists of either two or three distinct pyrometallurgical processing steps. Only enough sulfur should remain in the concentrates to insure that the copper will form a copper sulfide matte in subsequent processing operations. Sulfur in excess of this amount is eliminated by roasting or in the smelting furnace. The following primary reactions occur during roasting (the first two are thermal decomposition):

$$FeS_2 \rightarrow FeS + S$$

$$CuFeS_2 \rightarrow CuFeS + S$$

$$4FeS + 7O_2 \rightarrow 2Fe_2O_3 + 4SO_2$$

The sulfur formed in these reactions oxidizes to generate SO_2.

Copper matte, which is formed in the smelting furnace, is a mixture of molten iron oxide and copper sulfide. These mixtures are mixable over a wide range of compositions, so that oxidation of the iron alone will not separate iron from the concentrates; however, if silica is present, the iron oxide combines with it to form a liquid iron silicate slag that is immiscible with the sulfide phase. The slag phase floats on top of the matte layer. The primary smelting and refining reactions are as follows:[1]

Smelting: $FeS_2 + O_2 \rightarrow FeS + SO_2$

$FeS + 1\text{-}1/2O_2 \rightarrow FeO + SO_2$

$CuFeS_2 + 1\text{-}1/2O_2 \rightarrow FeO + Cu_2S + SO_2$

$3Fe_2O_3 + FeS \rightarrow 7FeO + SO_2$

Slag formation: $xFeO + ySiO_2 \rightarrow x(FeO)\cdot(SiO_2)_y$

Converting:

Slag blow: $2FeS + 3O_2 + SiO_2 \rightarrow 2FeO\cdot SiO_2 + 2SO_2$

Copper or finish blow: $Cu_2S + O_2 \rightarrow 2Cu + SO_2$

Side reaction: $Cu + 1/2O_2 \rightarrow CuO$

Matte is processed in a copper converter to remove the remaining impurities and form blister copper. About 1 to 2 percent of the sulfur entering a smelter is lost in slags, 3 to 4 percent is released as fugitive emissions, and the remainder is contained as SO_2 in the gases from roasters, smelting furnaces, and converters.[2] A total of about 1.8 Mg (2 tons) of SO_2 is generated for each 0.9 Mg (1 ton) of copper produced.

Although the three steps of copper smelting have the same functions in all smelters, there are large differences in the equipment used. Two types of roasters, four types of smelting furnaces, and two types of copper converters are used in this country.

Roasters--Four domestic smelters use multiple-hearth roasters.[3] These are tall, cylindrical devices through which concentrate is passed downward against a rising stream of hot air and combustion gases. Multiple-hearth roasters are used primarily by "custom" smelters that process a variety of concentrates from many sources.[4] In these operations, the roaster burns off only a fraction of the sulfur to adjust the composition of the concentrates to allow successful treatment in the smelting furnaces. Some multiple-hearth roasters are operated only intermittently with concentrates that necessitate their use. Off-gas typically contains less than 2 percent SO_2. With the exception of one installation, no roasters are currently equipped with controls for SO_2 emissions. Control at one installation is accomplished by blending the weak gas stream from the multiple-hearth roaster with a stronger gas stream for feed to an acid plant. Fugitive emissions are also a problem with multiple-hearth roasters.[5]

In contrast, fluidized-bed roasters are engineered and operated with the production of sulfuric acid equal in importance to the smelting of copper. These units are fed with special high-sulfur concentrates of uniform composition and produce a continuous stream of off-gas that is consistent in volume and contains 12 to 14 percent SO_2.[6] Four fluidized-bed roasters, each with an associated plant producing sulfuric acid, are operating in this country.[7] Emissions of SO_2 from fluidized-bed roasters consist only of the tail gas discharge of the sulfuric acid plants and minor fugitive discharges from occasional leaks.[8]

Smelting furnaces--The four types of smelting furnaces used in domestic primary copper production are the Outokumpu flash smelter, the Noranda continuous smelter, the electric smelter, and the reverberatory furnace. The first three types produce off-gas streams rich enough in SO_2 to be used for manufacture of sulfuric acid; the five copper smelters operating these furnaces use the gas for this purpose. The reverberatory furnaces operating at 11 of the 16 U.S. primary copper smelters, however, generate a weak off-gas stream that accounts for the greatest amounts of uncontrolled emissions of SO_2 in the nonferrous metals industries.[7]

The reverberatory furnace (shown in Figure 5.1-1) is a large horizontal chamber into which concentrate, flux, and various other materials are charged.[9] The furnace is heated by direct firing with natural gas, oil, or pulverized coal. During the firing of the furnace, sulfur in the concentrate burns to SO_2, which mixes with fuel combustion gases and large quantities of infiltrated cooling air. At about 1000°C (1832°F), the charge melts and undergoes the complex reactions to form copper matte, which is tapped

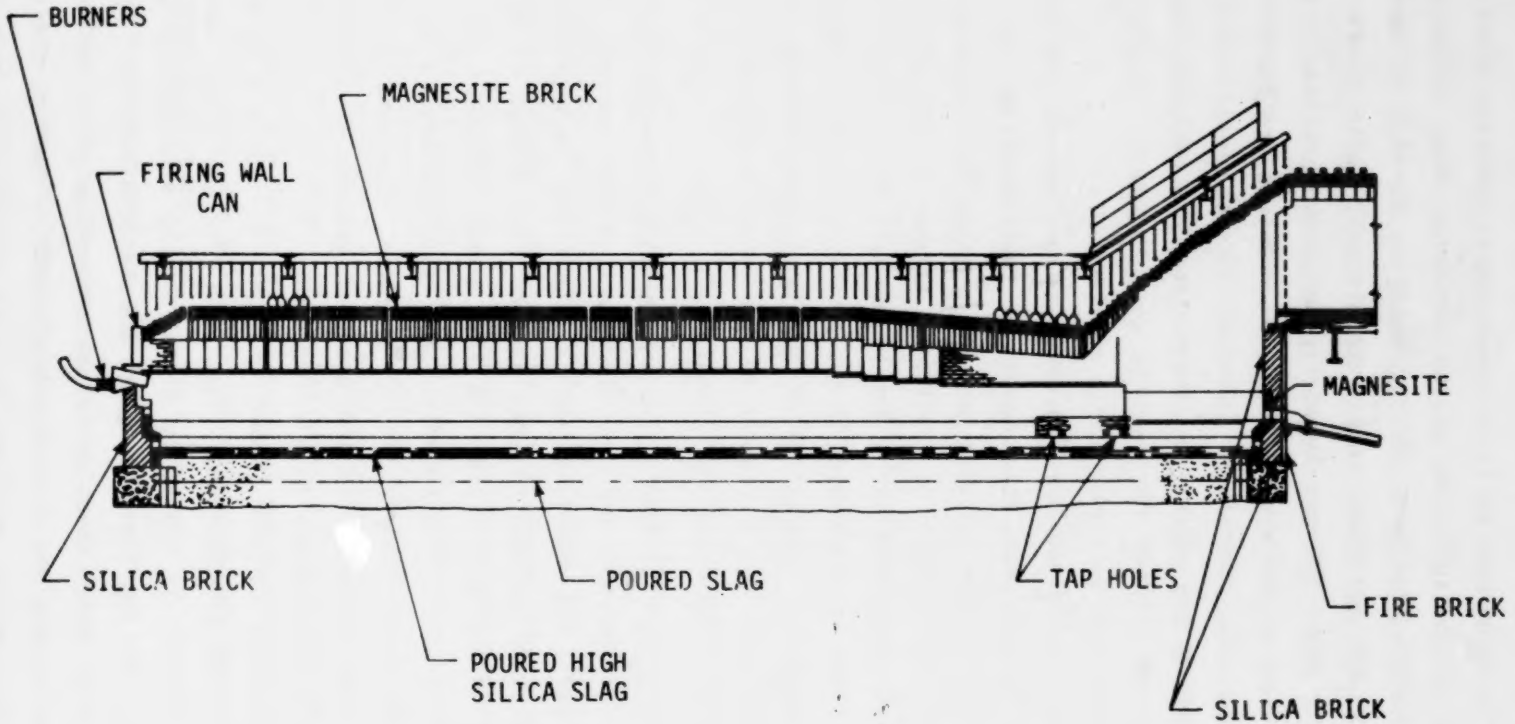
BURNERS
MAGNESITE BRICK
FIRING WALL CAN
MAGNESITE
SILICA BRICK
POURED SLAG
TAP HOLES
FIRE BRICK
POURED HIGH SILICA SLAG
SILICA BRICK

Figure 5.1-1. Section of reverberatory furnace.[9]

from the furnace and sent to the converters for further treatment.[10] The molten slag that also forms is discarded.

A typical charge contains 65 percent concentrate[9] with the balance composed of fluxes and reverts. The charge is fed into the furnace in small batches, resulting in wide variations in the SO_2 concentration and volume of the furance off-gases. From 20 to 50 percent of the sulfur in the concentrate is oxidized to SO_2 in the roasting step and 10 to 40 percent in the smelting step.[11] Concentration of the SO_2 in the furnace off-gases ranges from 0.5 to 3.5 percent, only occassionally exceeding 2.5 percent.[12] Some smelters have very large capacity furnaces, accepting up to 1800 Mg (2000 tons) per day.[9] A smelter of this size will generate about 300 Mg (330 tons) of SO_2 per day in the smelting furnace and roasters (if used). Where reverberatory furnaces are used alone or in combination with multiple-hearth roasters, all of the SO_2 generated is vented to the atmosphere because weak SO_2 stream control is not practiced in this country. One smelter using a fluidized-bed roaster to produce calcine for reverberatory smelting, however, reports a very low SO_2 emission rate from its furnace and an overall sulfur retention of 94 percent; this smelter uses only strong SO_2 stream control with a double-contact acid plant.

The electric smelter is similar to the reverberatory furnace, differing in that the heat is supplied by electricity rather than by combustion of fuel. By elimination of combustion gases, the SO_2 concentration in the off-gas is increased. The minimum and optimum SO_2 concentrations required for a conventional metallurgical-type single-contact sulfuric acid plant are 4 and 7 percent, respectively.[13] For a double-contact sulfuric acid plant these values are 7 and 9 percent.[13] Electric smelters are economical only in areas where electric power is relatively cheap and plentiful.

Both electric and reverberatory furnaces generate fugitive SO_2 emissions during tapping and charging operations. These amounts are small in comparison with the direct process emissions, and are estimated as approximately 5 percent and 7 percent of the direct process emissions.[14] Fugitive emissions are also released from leaks in the furnaces and auxiliary equipment.[15] No methods have been developed to measure these emissions.

The principal SO_2 emissions from the Outokumpu flash smelter and the Noranda continuous smelter are from the acid plant tail gases. There are, however, fugitive SO_2 emissions at tapping, slagging, and feeding ports. These emissions are estimated to contain 2.9 percent of the total sulfur feed to the furnace.[16] These units require a continuous and consistent feed of specially prepared concentrates, which are introduced along with pulverized flux. In the flash smelter, heat is added by preheating the inlet combustion air; the exhaust gases from fuel combustion are not mixed into the SO_2-rich gas stream. Flash smelter off-gas is a continuous stream containing up to 13 percent SO_2.[17] The Noranda continuous smelter burns fuel with oxygen-enriched air, which is mixed into the mineral feed.[18] Additional oxygen-enriched air is blown into the base of the Noranda unit, where it reacts with copper matte, partially converting it into impure blister copper. The Noranda unit was designed to function both as a smelting furnace and a converter; however, in its single U.S. application, a standard converter is also used to facilitate control of trace elements. The remaining sulfur in the matte is removed in the converter.[19] The Noranda furnace creates an off-gas containing about 16 to 20 percent SO_2,[20] but air infiltration around an exhaust hood reduces this concentration to 10 to 13 percent.[21] This furnace does, however, convert more than 90 percent of the input sulfur into a continuous-flow gas stream suitable for feed to an acid plant. Fugitive emissions during smelting are minimized because of the tight seal between the reactor and its hood.[22]

Converters--A copper converter is a horizontal, cylindrical vessel equipped with jets (tuyeres) through which air is blown. A batch of molten copper matte is charged into the converter through an opening on the top. The blowing of air through the matte oxidizes the remaining sulfur to SO_2 and converts the remaining iron into a slag, which is most often recycled to the smelting furnace. The product is blister copper. A converter is mounted on rollers and is rotated to pour out slag and blister copper through the charging port.

The two types of converters used in U.S. copper smelters differ mainly in the manner in which off-gas is discharged. In the Peirce-Smith converter, off-gas is vented through the charging port. This type is used in all but one of the U.S. smelters.[7] In the Hoboken converter, off-gas is drawn through a mechanical syphon attachment on one end of the vessel.

Converters have lower capacities than smelting furnaces; usually two or three converters are needed to process matte from one furnace. During the batch cycle, exhaust fans withdraw off-gas from each converter at a rate matched to the blowing rate. From a single converter the volume of off-gas is variable, and SO_2 concentration ranges from essentially 0 to 20 percent. Smelter operators therefore schedule the cycles of a group of converters so that the combined off-gas is relatively consistent. This combined stream contains 3.5 to 7 percent SO_2,[23] and all but three smelters use this stream for sulfuric acid manufacture.[7]

Copper converters are the principal source of fugitive SO_2 emissions into the atmosphere of the converter building. With Peirce-Smith converters, gases generated during blowing are pulled away from the converter through a hood mounted above the charging port.[24] Figure 5.1-2 shows that the primary hood is isolated when the converter is rolled out for either materials addition or skimming and pouring.[25] The Hoboken converter, with its attached syphon, does not lose suction when the converter is rotated but does lose SO_2 because of thermal and pressure imbalances in the converter, buildups in the syphon, and air currents above the charging port. These emissions can be minimized by proper operating practices.[26] As much as 3.5 percent of the SO_2 may be lost through fugitive emissions from a Peirce-Smith converter.

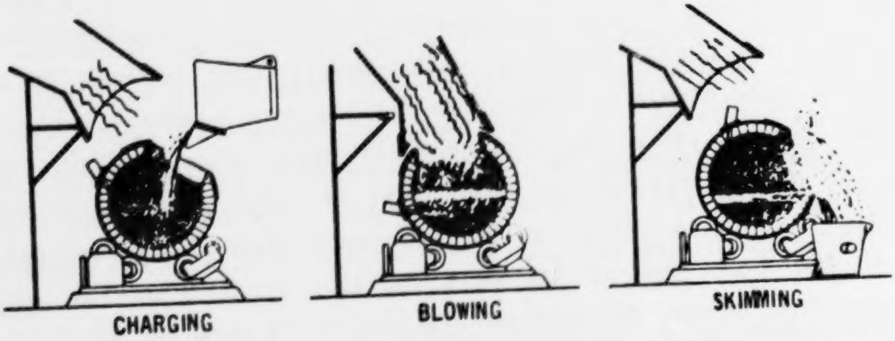

Figure 5.1-2. Peirce-Smith copper converter operation.[25]

5.1.1.2 Lead Smelters--

Lead ore is mined in two regions of the United States. Deposits in several western states usually include recoverable amounts of zinc and copper; some of these ores are processed first in a zinc smelter, and the sulfur-free residue is used as raw material in a lead smelter.[27] Ore from the rich deposits in Missouri contains no other recoverable metals. The raw material to smelters that process Missouri ore is a concentrate containing almost 90 percent galena (lead sulfide). Although actual emissions will vary depending on the sulfur content of the raw material, total SO_2 emissions from lead smelters is reported to be about 0.14 kg (0.3 lb) of SO_2 for each 0.45 kg (1 lb) of lead produced.[28]

Lead smelting begins with a sintering step to remove almost all of the sulfur by oxidation. The product from sintering is then processed in a blast furnace to produce lead bullion, an impure metal. Sintering is the only part of the lead smelting process that can emit large amounts of SO_2. Fugitive emissions of SO_2 also occur at the discharge end of the sinter machine, where the discharged material is broken into pieces. Low concentrations of SO_2 may occur in blast furnace off-gas. Processes that purify lead bullion emit no SO_2, although they do emit other pollutants.

The sinter machine, the principal source of sulfur oxides emissions, contains a horizontal metal belt that passes slowly through an enclosed combustion chamber. The charge material, a pelletized mixture of lead concentrate and flux, is spread on the belt and ignited with a gas flame. Burning of the charge during its passage through the chamber creates SO_2. Once ignited, the charge needs no supplemental fuel because it contains enough sulfide concentrate to furnish self-sustaining combustion.[29]

Off-gas from a sinter machine contains about 2 percent SO_2, which is too weak for use as feed to an acid plant.[30] With most sinter machines, however, the exit gases can be split into two streams. A strong gas stream evolved at the front end of the belt contains about 6 percent SO_2; four smelters use this stream for acid manufacture.[31] A weak gas stream from the back end of the belt contains about 0.5 percent SO_2.[32] Weak gas recycle is the only SO_2 control technique on weak gas streams in the United States. Two lead smelters do not divide the gases into strong and weak streams and practice no control of SO_2 emissions. Weak gas recycle is required by New Source Performance Standards.

The solids at the end of the belt are fused into a porous clinker (sinter), which is discharged from the belt into mechanical equipment that crushes and screens it to form particles of the proper size for use in the blast furnace. These operations release SO_2 from incomplete sintering and create fugitive SO_2 emissions. No emission factors are reported for this source because techniques for accurate measurement have not been developed.

In the blast furnace, crushed sinter, mixed with coke and flux are passed downward through a tall vertical rectangular column. Air is blown into the bottom of the furnace to burn the coke and create a high-temperature reducing environment that forms molten slag and lead bullion. Gases from a blast furnace, containing about 0.5 percent SO_2, are released without control of SO_2 emissions.[33]

5.1.1.3 Zinc Smelters--

Zinc ore is another sulfide mineral, and the raw material for a zinc smelter is a zinc concentrate made from zinc ores by processes that create no SO_2 emissions. Zinc concentrate contains up to 62 percent zinc, 32 percent sulfur, and variable amounts of iron, lead, cadmium, and copper.[34] Although a zinc smelter converts all the sulfur into SO_2, emissions are well controlled in this industry.

Two different methods are used to produce zinc metal from concentrate. The first step in both methods is to burn off almost all the sulfur by roasting. About 95 percent of the sulfur is converted into SO_2.[35] The product of roasting, called calcine, is an impure zinc oxide, which usually contains less than 0.3 percent sulfide sulfur.[36] Roasting is the only significant source of SO_2 emissions in a zinc smelter. Although actual emission will vary depending on the sulfur content of the raw materials, the process releases about 0.25 kg (0.55 lb) of SO_2 for each 0.45 kg (1 lb) of zinc produced.[37]

Calcine is processed either electrolytically or pyrometallurgically into zinc metal. The electrolytic process is entirely chemical and creates no SO_2 emissions.[38] Pyrometallurgical production may create low concentrations of SO_2 (0.1 to 2.4 percent) in off-gas from sintering machines.[39]

All U.S. zinc smelters now operate modern roasting equipment and use all the off-gas for manufacture of sulfuric acid. Two types of roasters are in use. These are the flash and the fluidized-bed roasters, both of which oxidize the sulfur while the concentrate particles are suspended in a moving stream of hot gases. Because zinc roasters need no supplemental fuel, the off-gas is not diluted with products from fuel combustion.[40] Roasters operate continuously and produce consistent volumes of an off-gas stream that usually contains 10 to 13 percent SO_2.[41] Because most zinc smelters are located in heavily industrialized regions, sulfuric acid is often a profitable byproduct.

5.1.1.4 Aluminum Smelters--

The processes of aluminum production are completely different from those of other nonferrous metal industries. Bauxite, the ore of aluminum, contains no sulfur and no other recoverable metals.[42] It is processed by chemical methods to alumina (aluminum oxide) in bauxite refineries. The only SO_2 emissions at refineries result from the combustion of fuel by calcining furnaces used to remove moisture from hydrated alumina. Calcined alumina is the raw material for aluminum smelters.

A smelter contains rows of electrolytic cells (shallow pots lined with carbon) in which carbon electrodes suspended above the pot serve as anodes. The pots serve as cathodes. Cryolite, a double-fluoride salt of sodium and aluminum (Na_3AlF_6), is used as an electrolyte and a solvent for alumina.[43] Alumina is added to and dissolves in the molten cryolite bath. The cells are operated between 950° and 1000°C (1742° and 1832°F) with heat that results from the electrical resistance between the anode and the cathode.[43] During the reduction process, the aluminum is deposited at the cathode where, because of its heavier weight, it remains as a molten metal layer beneath the cryolite. The byproduct oxygen migrates to and combines with the consumable carbon anode to form carbon dioxide and carbon monoxide, which continually evolve from the cell.[44] Additionally, the gas stream contains evolved hydrogen fluoride and fluoride-containing particulate matter.

The reduction cells in use for aluminum production in the United States are of two basic types, prebake and Soderberg. There are two types of

Soderberg cells that are designated according to the manner of mounting the stud in the carbon anode: vertical stud Soderberg (VSS) or horizontal stud Soderberg (HSS).

Prebake cells are so named because the anodes are preformed and then baked in a separate facility often referred to as an anode bake plant. The anodes are then mounted in the cell and are consumed in the aluminum production. The anode butts, which remain after the anode is consumed, are recylced for use in the preparation of new anodes.

In the Soderberg process, continuously formed, consumable anodes are used. The anode paste is baked by the heat generated in the reduction cell.

The primary source of sulfur oxide emissions in aluminum production is the sulfur in the coke (normally petroleum coke) and the coal tar pitch binder used to produce the anodes. In the prebake process, the combustion fuel to bake the anodes may be a significant SO_2 emission source. Petroleum coke usually contains 2.5 to 5 percent sulfur, but may vary from 1.5 to 7 percent sulfur.[45,46] Pitch normally contains about 0.5 percent sulfur.[46] The sulfur content of the coke depends on the crude petroleum stock and the tendency of the sulfur to concentrate in the still bottoms at the refinery and thus in the coke. The trend appears to be toward coke with higher sulfur content; however, marketing factors and price may affect this trend.[47] The production of aluminum by electrolytic reduction (the prebake and Soderberg processes) consumes 0.5 to 0.6 kg carbon anode/kg aluminum produced (0.5 to 0.6 lb carbon anode/lb aluminum produced).[48]

As the coke is processed (during prebake) or consumed in the reduction cell, sulfur oxides are released. The emissions include those from the anode prebake operation (prebake), the "primary" emissions (which are captured by the pot hood exhaust system), and the "secondary" emissions (which escape the primary exhaust system and exit through the roof monitors). The great majority of SO_2 emissions are collected by the pot hood exhaust system.

One source reports uncontrolled SO_2 emissions from anode bake plants range from 5 to 47 ppm, which is 0.7 to 2 kg SO_2/Mg aluminum produced (1.4 to 4 lb SO_2/ton aluminum produced).[49] Other data indicate that emissions are in the range of 0.09 to 1.7 kg SO_2/Mg aluminum produced (0.18 to 3.4 lb SO_2/ton aluminum produced).[49]

The total amount of SO_2 generated per unit of aluminum produced is essentially the same for the prebake, VSS, and HSS cases. The "primary" cell hooding configuration for collection of process fumes is affected by the characteristics of the different cell types.[50] There are two types of prebake cells, center-worked prebake cells (CWPB) and side-worked prebake cells (SWPB), as well as the two Soderberg processes, VSS and HSS, which are in use by the domestic aluminum industry. Information from seven primary aluminum plants indicates the following:[51]

Cell type	Primary hood collection efficiency, %	Primary collector exhaust rate, Nm^3/kg Al (10^6 scf/ton Al)
CWPB	65 to 98 (average 88)	128 to 158 (4.11 to 5.05) [average 141 (4.51)]
SWPB	85	107 (3.44)
VSS	81	21 (0.67)
HSS	80 to 95 (average 90)	158 to 245 (5.06 to 7.85) [average 209 (6.68)]

This information indicates that the gas volume associated with the production of a fixed amount of aluminum is in the range of 5 to 12 times (average 8 times) greater for CWPB, SWPB, or HSS than for VSS. Consequently the concentration of SO_2 in a volume of exhaust gas in the primary collector system can be expected to be about 8 times greater for a vertical stud Soderberg unit than for other units.

Reported data on uncontrolled "primary" exhaust system SO_2 emissions are as follows:[52]

Unit	Source	SO_2 concentration, ppm	Total SO_2 emissions, kg SO_2/Mg Al (lb SO_2/ton Al)
Prebake cell	A	5	Not reported
	B	Not reported	20.9 to 23.4 (41.7 to 46.8) [average of 22.4 (44.8)]
	C	Not reported	30 (60) [3% S in the coke]
Vertical stud Soderberg cell	A	80	Not reported
	B	200 to 300	17.5 to 25 (35 to 50)
	C	200 (average)	Not reported

The trend in construction of new aluminum plants is toward prebake systems. A major factor influencing this trend is the lower power requirement of the prebake cell compared with Soderberg cells.[53] It is reported that 9 of the 11 aluminum plants opened since 1960 are of the prebake type, and 99 percent of the 324 Gg (357,000 tons) capacity added since 1973 has been at prebake facilities.[54] Of the industry's total annual capacity of 4.8 Tg (5.3 million tons) prebake units account for 68 percent, HSS plants account for 20 percent, and VSS plants account for 12 percent.[54]

5.1.1.5 Molybdenum Smelters--

The raw material for a molybdenum smelter is an ore concentrate that usually contains about 90 percent molybdenum disulfide. This is produced at mines operated specifically for molybdenum production and also is a byproduct of copper mining and concentrating operations. The United States is a principal world supplier of molybdenum, which is used mostly as an alloying additive to steel.[55] Only a small fraction is processed to metallic molybdenum.

The molybdenum smelting process is one of the simplest nonferrous metal operations. Technical-grade molybdic oxide is made by roasting the concentrate to remove essentially all sulfur as SO_2, a process similar to the roasting of zinc concentrates.[56] Most molybdic oxide is sold to the steel industry in this form. Some is converted into other products by processes that do not generate SO_2 emissions.[57]

Multiple-hearth roasters are the most common type of equipment used in this process.[56] Supplemental fuel is necessary only during startup. Because of the use of large amounts of infiltration air for gas cooling and high excess air ratios in the roaster, the roaster off-gas contains only about 1.3 percent SO_2 and cannot be used for sulfuric acid manufacture without supplemental sulfur burners. By chemical balance, production of 1.17 kg (2.58 lb) of molybdic oxide, equivalent to 1 kg (2.20 lb) of elemental molybdenum, creates at least 1.33 kg (2.95 lb) of SO_2.

5.1.2 Control Techniques

In the nonferrous metals industry, controls are being applied to all strong gas streams that contain about 3 percent SO_2 or more. Controls are rarely applied in this country to weak gas streams containing less than 3 percent SO_2. The techniques available for SO_2 control differ depending on whether the stream is strong or weak.

In all the facilities that generate strong gas streams, this gas is used as feed to a sulfuric acid plant. This control technique is used in all zinc smelters, two molybdenum smelters, four lead smelters, and 14 copper smelters. Both single- and double-contact acid plants are in use; Section 5.5 provides details of this control technique.

In Japan and Sweden weak gas streams are controlled by wet scrubbing. One U.S. copper smelter attempted scrubbing a stream of marginal SO_2 concentration (about 2 percent) with an organic liquid, dimethylaniline (DMA).

5.1.2.1 Description--

Copper industry--Copper smelters create strong SO_2 gas streams from the operation of electric smelting furnaces, fluidized-bed roasters, most converters, and (in two modernized smelters) newer types of smelting furnaces. The accepted industry practice for control of strong SO_2 gas streams is the contact sulfuric acid plant or conversion to liquid SO_2. Table 5.1-1 summarizes the process and SO_2 control equipment of the 16 U.S. copper smelters. Except for the DMA absorption unit at the Phelps-Dodge Ajo smelter, which did not operate properly and is now shut down, all SO_2 control equipment listed is applied to gas streams containing at least 3 percent SO_2.

The DMA absorption system is a cyclic-regenerative process that incorporates an absorber with trays on which most of the incoming SO_2 is absorbed in a countercurrent stream of DMA. The residual SO_2 in the gases is scrubbed with a weak sodium carbonate solution to give sodium sulfite or sodium bisulfite. Liquid sulfur dioxide is recovered as a product, and its absorbent is regenerated and recycled through the system.[58] Typical SO_2 emissions from a DMA unit may be in the 2000- to 3000-ppm range.[59] Cities Service Company operates two DMA absorption systems rated at 36 and 50 Mg (40 and 55 tons) of liquid SO_2 per day at Copperhill, Tennessee. The feed stream for the DMA system is 7.6 percent SO_2, and is a mixture of off-gases

TABLE 5.1-1. SUMMARY OF PROCESS EQUIPMENT AT COPPER SMELTERS IN THE UNITED STATES[7]

Smelter	Emitting equipment	Off-gas flow rate, Nm^3/s (scfm)	Particulate control equipment	SO$_2$ control equipment	Stacks, m (ft)	Comments
Kennecott Hayden	Fluid bed roaster	15 (31,000)	2 Banks of cyclones, 4 Primary, 4 secondary Venturi scrubber Peabody scrubber ESP	Double contact acid plant for roaster and conv. off-gas 862 Mg/day (950 tons/day)	30 (100) (Roaster and conv.) 183 (600)	
	Reverberatory furnace	61 (130,000)	ESP			
	3 Converters	24 (50,000)				
			Peabody scrubber Mist precipitator Mist eliminator Roaster and converter			
Phelps Dodge Morenci	Fluid bed roaster	11 (24,000)	Scrubber	Acid plant 544 Mg/day (600 tons/day)	184 (605)	Roaster treats only 35% of input materials
	5 Reverberatory furnaces	133 (282,000)	ESP's	Acid plant 1880 Mg/day (2070 tons/day) 2270 Mg/day (2500 tons/day) (max)	184 (605)	
	9 Converters	274 (580,000) (max)	ESP's Gas cleaning		184 (605)	
ASARCO El Paso	4 Multihearth roasters	27 (56,858) 49 (103,255) 13-25 (28,334-52,430)	Spray chamber ESP	Acid plant	252 (828) (roaster and reverb.)	
	3 Reverberatory furnace converters	27 (56,300)	Spray chamber ESP	Double contact (conv.) acid plant 450 Mg/day (500 tons/day)	30 (100)	
			Baghouses		172 (563)	Arsenic circuit
ASARCO Tacoma	6 Multihearth roasters					
	10 Multihearth roasters	14-33 (30,000-70,000)	Plate and pipe precipitators			
	2 Reverberatory furnaces	19-47 (40,000-100,000)				
	4 Converters	0-47 (0-100,000)	2 Spray chambers 2 ESP's 6 Scrubbers 2 Mist cottrells	Acid plant 180 Mg/day (200 tons/day) DMA liquid SO$_2$	305 (1000)	
ASARCO Hayden	12 Multihearth roasters	47 (100,000)	Settling chamber ESP			
	2 Reverberatory furnaces	104 (220,000)	Spray chamber 2 Cyclones			
	5 Converters	14-19 (29,000-40,000)	Spray chamber ESP Scrubbing tower Mist precipitator	Acid plant 680 Mg/day (750 tons/day) (nominal)		

TABLE 5.1-1 (continued)

Smelter	Emitting equipment	Off-gas flow rate, Nm³/s (scfm)	Particulate control equipment	SO_2 control equipment	Stacks, m (ft)	Comments
Phelps Dodge Douglas	24 Multihearth roasters	132-142 (280,000-300,000) (from ESP)	ESP	No SO_2 control	152 (500) (roaster and reverb.)	
	3 Reverberatory furnaces	85 (180,000) (from ESP)	ESP			
	5 Converters	99-125 (210,000-265,000) (from ESP)	ESP		172 (563)	
Phelps Dodge Ajo	3 Reverberatory furnaces	33 (70,200) (from ESP)	ESP	DMA absorption, liquid SO_2 - 38,000 Mg/yr (41,508 tons/yr) Acid plant 540 Mg/day (600 tons/day)	110 (360)	
	3 Converters		ESP			
White Pine Michigan	Rotary dryer	14 (30,000) (from scrubber)	Scrubber			
	2 Reverberatory furnaces	76 (160,000) (from ESP)	ESP	No SO_2 control	154 (504)	
	2 Converters	20 (43,000)	No control			
Magma San Manuel	3 Reverberatory furnaces	165-212 (350,000-450,000) (from ESP)	ESP		157 (515)	168-m (550-ft) stack receives bypass from ESP
	6 Converters	73-94 (154,000-200,000) (from ESP)	ESP Scrubber - Cooler	Acid plant - 2200 Mg/day (2400 tons/day) (conv.)	2 at 61 (200) 168 (550)	
Kennecott Hurley	Rotary dryer	28 (60,000) (from scrubber)	Cyclone Scrubber		155 (510)	
	2 Reverberatory furnaces	71-94 (150,000-200,000)	ESP			
	4 Converters (3 Operating)	12 (26,000) per converter	3 ESP's Peabody scrubber	Double contact acid plant 540 Mg/day (600 tons/day) (avg.) 820 Mg/day (900 tons/day) (max)	61 (200) 191 (625)	(bypass from scrubber)
Kennecott McGill	Reverberatory furnace	99 (209,000)	Cottrell plant	No SO_2 control	229 (750)	450 Mg/day (500 tons/day) acid plant and ESP for reverberatory furnace and converters under construction at writing of February 1976 EPA report
	Converters	83 (176,000)	Multicyclone			
Anaconda Montana	Fluid bed roaster	28 (60,000)	Cyclone spray chamber, baghouse	Double contact acid plant, 35 Nm³/s (75,000 scfm) (max)	178 (585) (main) 53 (175) (acid plant)	
	3 Electric furnace	7 (15,000)				
	3 Converters	80 (170,000)				

TABLE 5.1-1 (continued)

Smelter	Emitting equipment	Off-gas flow rate, Nm³/s (scfm)	Particulate control equipment	SO_2 control equipment	Stacks, m (ft)	Comments
City Services Copperhill	Fluid bed roaster	5 (10,000)	Cyclone Peabody scrubber Swenco scrubbers ESP's	Three double contact acid plants	61 (200)	
	2 Electric furnace converters	3 (7,000) 1 (3,000)				
Inspiration Miami	Rotary dryer		Cyclones, baghouse	Double contact acid plant 1200 Mg/day (1330 tons/day)	61 (200)	
	Electric furnace	9 (20,000)	2 Cyclones ESP Scrubbing tower, mist precipitators			
	5 Converters	33 (70,000)	5 Cyclones 3 ESP's			
Phelps Dodge Hidalgo	Rotary dryer		ESP	Two acid plants Total gas volume emitted 65 Nm³/s (138,200 scfm)	61 (199) 183 (600) 61 (200)	For acid plant For furnace For power plant emissions
	Flash furnace		ESP			
	Slag furnace		Scrubber			
	3 Converters		ESP			
Kennecott Utah	2 Rotary dryers		Cyclones, scrubbers		366 (1200)	Off-gases from the smelting vessels and the converters are treated in the acid plant and emitted through the 366-m (1200-ft) stack
	3 Noranda reactors		Cyclones, 6 ESP's	Acid plant		
	4 Converters		ESP	Acid plant		

from electric furnaces and fluidized-bed roasters. The absorbers could be operated to achieve a concentration as low as 1500 ppm SO_2 in the treated exit gas.[60] ASARCO, Inc., at Tacoma, Washington, uses DMA absorption to recover SO_2 from smelter off-gases that have (or can be upgraded to have) SO_2 concentrations in the range of 4 to 10 percent.[58] The system is rated at 180 Mg (200 tons) of liquid SO_2 per day.

Although no estimates are reported, a high percentage of the SO_2 generated by the industry is now being converted into sulfuric acid. Of the 16 domestic copper smelters of all types, 14 are equipped with one or more acid plants.[7] Total acid plant capacity is over 6.1 Tg (6.7 million tons) annually.[61]

Typical SO_2 emissions from a single-contact sulfuric acid plant operating on a strong SO_2 stream from a copper smelter may be in the 2700-ppm range.[62] Typical SO_2 emissions from a double-contact sulfuric acid plant operating on a strong SO_2 stream from a copper smelter may be expected to be in the 400- to 500-ppm range.[63]

Weak SO_2 streams are created from the operation of all reverberatory furnaces, some converters, and most multiple-hearth roasters in the United States. The acid plant tail gas also contains unreacted SO_2, and fugitive emissions from converters and reverberatory furnaces create a dilute SO_2 stream in the ventilation air of buildings. No control of SO_2 emissions from weak streams is practiced in this country.

Use of the SO_2 from these weak SO_2 gas stream sources for acid manufacture is limited by the technical requirements of a conventional acid plant. For efficient performance, the gas delivered to the plant must be consistent in volume and SO_2 content and must consistently contain from 4 to 9 percent SO_2.[2]

In foreign smelters, control of weak stream SO_2 is practiced. Table 5.1-2 summarizes the process and control equipment used by 8 of the 14 copper smelters in Japan. This table indicates that weak streams, primarily from acid plant tail gases, are scrubbed with both lime and caustic solutions in nonregenerable FGD equipment.[64] In addition, the Onahama Smelting and Refining Company of Japan used a regenerable magnesium oxide (MgO) scrubbing system and still uses a nonregenerable lime scrubbing system to treat exhaust gases from a reverberatory furnace containing 2 to 3 percent

TABLE 5.1-2. SMELTING AND SO_2 EMISSION CONTROL PRACTICE[64]

Smelter	Copper capacity, 1000 mg/yr	Smelting process	Off-gas SO_2, %	Furnace gas treatment	Acid plant tail gas scrubber	Sulfur capture, %
Ashio: Furukawa Mining Co.	40	Flash furnace P-S converters	a	ST acid plant		91
Hitachi: Nippon Smelting Co.	150	Flash furnace, O_2 enriched P-S converters	10-12 4-6	DT acid plant ST acid plant	None None	97
Kosaka: Dowa Mining Co.	60	Flash furnace P-S converters	8-10 4-6	ST acid plant ST acid plant	CaO slurry CaO slurry	99
Naoshima: Mitsubishi Smelter Co.	150	Fluid-bed roaster Reverberatory furnace P-S converters	11 b c	DT acid plant	None	98
(2 systems)	50	3-furnace continuous	10	ST acid plant	CaO slurry	
Onahama: Onahama Smelting and Refining Co.	240	Reverberatory furnace P-S converters	2-2.5 7-9	1/2 to MgO scrubber, then strong SO_2 to DT acid plant, 1/2 to CaO scrubber ST acid plant	NaOH solution CaO slurry	99
Saganoseki: Nippon Mining Co.	150	Flash furnace O_2 enriched P-S converters	10-12 4-6	DT acid plant ST acid plant	None NaOH solution	97
Tamano: Hibi Kyodo Smelting Co.	80	Flash furnace P-S converters	7-8 a	DT acid plant	None	99
Toyo: Sumitomo Metal Mining Co.	120	Flash furnace P-S converters	7-8 a	ST acid plant	NaOH solution	99

DT = Double train. P-S = Peirce-Smith. ST = Single train.

[a] Combined with flash furnace gas.
[b] Combined with continuous furnace gas.
[c] Combined with roaster gas.

SO_2.[65] The MgO scrubbing system produced a strong SO_2 stream, which was subsequently used to manufacture sulfuric acid. The lime scrubbing system produces gypsum as a byproduct.[65] The domestic copper industry has not yet adopted control of weak SO_2 streams (i.e., <2 percent) by nonregenerable liquid scrubbing.

Revision of production methods may be an economically valid method of SO_2 control since adoption of newer equipment also usually leads to significant reductions in energy consumption and production costs. A principal source of SO_2 is the reverberatory furnace, which has poor thermal efficiency. Reverberatory furnaces consume about 90 percent of all energy used in copper smelting[4] and operate at less than 25 percent efficiency.[66]

It is possible to replace the reverberatory furnaces with other types of smelting equipment and thereby to upgrade the concentration of SO_2 in the furnace off-gases. Alternative processes are the flash smelter, the Noranda furnace, and several other systems used abroad.[67] All of these claim or have demonstrated consistent production of off-gas suitable for acid plant feed, and energy consumption from 50 to 70 percent of that used by the reverberatory furnace. Oxygen enrichment will further lower fuel requirement.[68] None, however, is adaptable to all grades and types of concentrates, and most produce slag that contains too much copper to be discarded without further treatment.

The Noranda and similar continuous furnace designs not only permit simplified control of smelting furnace off-gas, but also minimize fugitive emissions of SO_2 from copper converters. As used in the United States, the Noranda furnace produces a high-grade matte (>60 percent copper), which requires the use of a converter, although with much-reduced potential for fugitive losses.[69]

The size of these advanced copper manufacturing systems almost always precludes retrofit at an existing smelter. It usually is necessary to build new buildings and relocate auxiliary equipment such as cranes. Because more SO_2 is captured, the new acid plants usually must be added and markets for the additional acid must be found. Auxiliary slag cleaning plants are also needed. Two U.S. primary copper producers have elected to do this and have achieved substantial reductions in SO_2 emissions.

Replacement of Peirce-Smith converters with the Hoboken type is also possible, although the extra space required complicates retrofitting. Operation of the Hoboken converter calls for special auxiliary equipment and different operating procedures. Properly operated and equipped with necessary hoods, fans, and process controls, a Hoboken converter can prevent the escape of more fugitive SO_2 emissions than a Peirce-Smith converter.[70] Because fugitives are weak SO_2 emissions and off-gas is a strong SO_2 stream, the Hoboken converter can permit more complete control of overall emissions.

The ultimate process change is abandonment of the copper smelter through the adoption of hydrometallurgy.[71] In hydrometallurgical systems, chemicals leach sulfide copper ores to extract the copper content, which is then electrochemically converted into metal. The sulfur in the ore is changed into either elemental sulfur or the sulfate ion, neither of which is an atmospheric pollutant. Emission of SO_2 is completely eliminated. Interest in copper hydrometallurgy appears to be declining, however, because these processes consume more energy than pyrometallurgical methods and also present formidable problems of solid and liquid waste disposal.[72]

Lead industry--The principle source of SO_2 emissions in the lead industry is the sinter machine in which the lead sulfide concentrate (PbS) is converted into an oxide or sulfate form. During sintering approximately 85 percent of the concentrate sulfur is removed as SO_2.[73] A hood is generally installed over the sinter machine to capture the SO_2 emissions. The emissions may be captured in separate effluent streams (one with strong SO_2 concentration from the feed end and one with weaker SO_2 concentration from the discharge end) or in a combined stream; or only the strong off-gas stream from the feeder end may be captured. One control technique that concentrates essentially all of the SO_2 emissions into a single stream strong enough for sulfuric acid manufacture is the use of the updraft-type sinter machine with a weak SO_2 gas stream recycle system. In this system, air is passed twice through the sinter machine. Combustion air is drawn from a hood near the sinter breaking equipment, thereby capturing fugitive SO_2 emissions from this source. The air is first passed through the back end of the machine, forming a weak SO_2 gas stream. The stream is captured by a high-temperature fan and recycled through ductwork to the front end of the machine. The strong gas stream thus produced contains all of the SO_2

generated and is strong enough for manufacture of sulfuric acid. This system is installed at one U.S. lead smelter and has been used at foreign smelters for many years.[74] It has been reported that the use of gas recirculation will decrease the production capacity of an updraft sintering machine compared with a similar machine without gas recirculation.[75]

The alternative to this system is liquid scrubbing, which is the technique applicable to acid plant tail gas and blast furnace off-gases. The Cominco ammonia absorption process has been used with very good recovery to treat process off-gases having SO_2 concentrations as low as 0.5 percent. In this process, the SO_2-laden off-gases are treated by an ammonium sulfite solution in a countercurrent manner. The ammonium bisulfite solution generated in the absorber is acidified with sulfuric acid to produce a concentrated (25 percent) SO_2 gas stream. The dilute ammonium sulfate stream is treated in an evaporator to produce a granular product, which is used as fertilizer.[76] Cominco has operated ammonium sulfite-bisulfite scrubbing systems at their smelter located at Trail, B.C., Canada, since the 1930's. The ammonia scrubbing systems serve Dwight-Lloyd lead sintering machines and zinc roasters.[76] The SO_2 concentration of inlet gases to the Dwight-Lloyd lead sintering machine absorption system ranges from 0.3 to 2.5 percent; however, fumes cause major visible emission problems at this installation.[76] Some Japanese lead smelters scrub blast furnace off-gas and weak streams from the sinter machine; lime and sodium compounds are in use.[77] Recently a study has been made to define alternatives applicable to control SO_2 emissions from a lead smelter and zinc plant of the Bunker Hill Company in Kellogg, Idaho.[78] The study concludes that three FGD processes (aluminum sulfate-DOWA, citrate, and ammonium sulfate) are technically feasible to treat lead smelter sinter machine weak or strong stream off-gases.[78]

Zinc industry--The domestic zinc industry has demonstrated an acceptable SO_2 control technique, and equipment that can give adequate control is installed at all U.S. zinc smelters. The control technique employed is use of the SO_2 for manufacture of sulfuric acid. The most profitable smelter operations remove essentially all sulfur from ore concentrate by roasting and use an energy-efficient type of roasting equipment. The waste gas stream thus produced is ideal for use in acid manufacture.[79] Another option is the manufacture of liquid SO_2 if a market for this material is available.

The largest emission of SO_2 from a zinc smelter should be from the tail gas of the sulfuric acid plant. If the plant is properly designed and operated, it should remove about 99 percent of the SO_2 fed to it and the exit gases should contain no more than 0.05 percent SO_2 (as indicated in Section 5.5).

Fugitive emissions of SO_2 may result from leaks in roasters and from equipment that transports calcine. These emissions can be controlled by proper maintenance and by recycling the polluted air to the roaster as part of the combustion air.

Pyrometallurgical plants will probably continue to emit very small amounts of SO_2 in sinter machine off-gas. These plants must avoid over-roasting, which causes loss of zinc in subsequent processing steps.[29] With adequate process controls the off-gas should contain much less than 2 percent of the total sulfur content. Sodium, lime, and zinc compounds are used to scrub sinter machine off-gas at some Japanese zinc smelters[80] but not in this country.

Aluminum industry--The most significant air pollutants emitted by aluminum smelters are fluorides and particulate matter. In general, SO_2 emissions have been considered relatively insignificant,[81] but two control techniques can be applied if control is required. With all process designs, reducing the sulfur content of the anode coke will result in reduced sulfur oxide generation. In addition, flue gas desulfurization (FGD) has been demonstrated on VSS-type processes.

The sulfur content of petroleum coke is related to the quality of the crude oil from which it is produced. Good quality feedstocks for anode coke include thermal tar, cat craker slurry, decanted oil, and coal tar pitch. Poor feedstocks include vacuum residuals and derivatives of high-sulfur crudes.[46] In 1979, it was projected that supplies of low-sulfur anode coke derived largely from doemstic crude were expected to be available for the next 5 to 10 years. Future supplies of low-sulfur anode coke will depend primarily on the availability of low-sulfur foreign crude. Although low-sulfur coke may be currently available, one petroleum coke manufacturer reported in 1978 that low-sulfur coke commanded a price four to five times that of high-sulfur coke.[47]

Essentially all the SO_2 emissions from the Soderberg process and over 90 percent of the SO_2 emissions from the prebake process occur in the reduction cell.[52] It has been estimated that primary cell collection systems can capture 80 to 95 percent of the cell gases.[82] The remainder escapes through roof vents; or a portion may be collected by secondary controls. Therefore, it may be estimated that 70 to 95 percent of all the SO_2 emitted in aluminum production exits from the process through the primary collection system.

Older emission control systems in the aluminum industry consist of water scrubbers designed for simultaneous removal of fluorides and particulate matter from the primary exhaust system. Although designed to capture fluorides, these scrubbers also absorbed some SO_2, which was discharged with the scrubber overflow as a wastewater constituent. One such wet scrubber followed by a wet ESP at a VSS plant was reported to have an SO_2 control efficiency of 70 percent.[83]

At newer aluminum plants, wet scrubbers are being replaced by dry scrubbers, which use alumina as an adsorbent. Dry systems have the advantage of adsorbing gaseous fluorides and mechanically capturing particulate matter. These systems, however, are ineffective in controlling SO_2 because any SO_2 captured is eventually released through the primary or secondary exhaust systems.

Dry scrubbing systems allow the captured fluorides to be returned to the cryolite bath without further processing. At most aluminum plants using dry scrubbers, all of the alumina fed to the potline is first routed through the scrubbing system. In addition to removing fluorides, the alumina also adsorbs some SO_2; however, adsorbed SO_2 is immediately re-emitted when the alumina reaches the reduction cell. Most of the SO_2 is once again removed from the hooded cell and exhausted through the primary collection system, and the remainder escapes into the cell room.

Because of the lower gas flow rates in the primary collection system and higher SO_2 concentrations, for the use of anode coke of a given sulfur content, FGD is more feasible for VSS processes than HSS or prebake processes. Because of greater primary exhaust volumes and the resultant dilute

SO_2 concentrations, HSS and prebake plants would require much larger FGD capacities than a VSS plant.[84] The VSS off-gases contain SO_2 concentrations 6 to 10 times higher than those associated with other processes.[83]

A sodium-based FGD system has been installed downstream of the dry fluoride/particulate matter scrubber at each of the Martin Marietta Aluminum Company's VSS plants in The Dalles, Oregon, and Goldendale, Washington. The installation is in response to a determination of Best Available Control Technology (BACT) as required by Prevention of Significant Deterioration (PSD) regulations, and operating permits require 70 percent SO_2 removal to achieve an emission limitation of 9.5 kg SO_2/Mg of aluminum produced (19 lb SO_2/ton of aluminum). The supplier of the control systems designed and guaranteed the adsorbers for 90 percent removal (450 ppm SO_2 inlet, 45 ppm SO_2 outlet). The SO_2 inlet concentration may vary from 150 ppm SO_2 to 450 ppm SO_2 with an average expected of 300 ppm SO_2. The systems are designed to treat 94 m^3/s (200,000 cfm) of gas at 121°C (250°F). The cost was approximately \$2 million per system or \$21,300/m^3 per s (\$10/scfm).[85] The application of FGD to HSS or prebake processes has not been demonstrated.

Sulfur oxides not collected by the primary system escape through the cell room ventilator. Several aluminum smelters are now equipped with secondary scrubbers to treat the ventilation air, but these are typically water spray screens designed to capture fugitive fluoride emissions.[86] The application of FGD to these weak SO_2 gas streams has not been demonstrated.

Molybdenum industry--The roasting of molybdenum concentrate has been examined less intensively than the processes of other nonferrous industries. Molybdenum is made in much smaller quantity; the industry generates less than 2 percent of the amount of SO_2 generated by the copper industry.

No reports describe potential process modifications to permit the use of roaster off-gas for manufacture of sulfuric acid. Both the copper and zinc industries have replaced multiple-hearth roasters with other equipment that not only creates high-concentration SO_2 streams but also reduces energy consumption. This may also have been accomplished with the aid of supplemental sulfur burners at the two molybdenum smelters that sell sulfuric acid, although no published information is available.

A recent study of one of the larger molybdenum roasters indicates the possible use of a lime-based, nonregenerable SO_2 scrubber to control these gases. Union Carbide and Duvall employ byproduct colloidal lime slurry to remove SO_2 from the off-gas of a small molybdenum roaster in Bishop, California.[87] A lime slurry sulfur dioxide scrubbing system is also being used to control off-gases from two multihearth roasters processing molybdenum copper ore at the Duval Sierrita Company processing plant near Tucson, Arizona.[88] Unless the production process used in most molybdenum smelters is modified, nonregenerable scrubbing may be the only feasible control method.

5.1.2.2 Control Cost--

Cost curves have been generated for the capital and annual operating costs of double-contact/double-absorption sulfuric acid plants.[89] The capital costs are presented in Figure 5.1-3, and annual operating costs are presented in Figure 5.1-4. Details of the estimated control costs applicable to electric smelting, flash smelting, and reverberatory smelting are also available.[90]

A recent study sponsored by the EPA has calculated capital and annual costs of installing wet scrubbers on weak SO_2 gas streams from a "typical" reverberatory furnace and copper smelter converters.[91] No systems of this type are currently in use in the United States. The costs of two nonregenerable scrubbing systems (lime and limestone) and two regenerable systems (magnesium oxide and sodium citrate) were calculated for several streams, two of which are

- 98,900 Nm^3/h (58,200 scfm) at 1 percent SO_2
- 76,500 Nm^3/h (45,000 scfm) at 1.4 percent SO_2

A summary of the cost data adjusted to mid-1979 is presented in Table 5.1-3. Data on regenerable systems are shown as two separate costs: one for the scrubbing units and one for the SO_2 drying and liquefication equipment. Detailed estimates of capital and annual costs for these FGD systems treating different off-gas flow rates are available.[91]

Actual costs would be somewhat higher than those shown, since actual gas streams from the principal uncontrolled sources (the reverberatory furnaces) result from cyclic operations and therefore vary widely both in

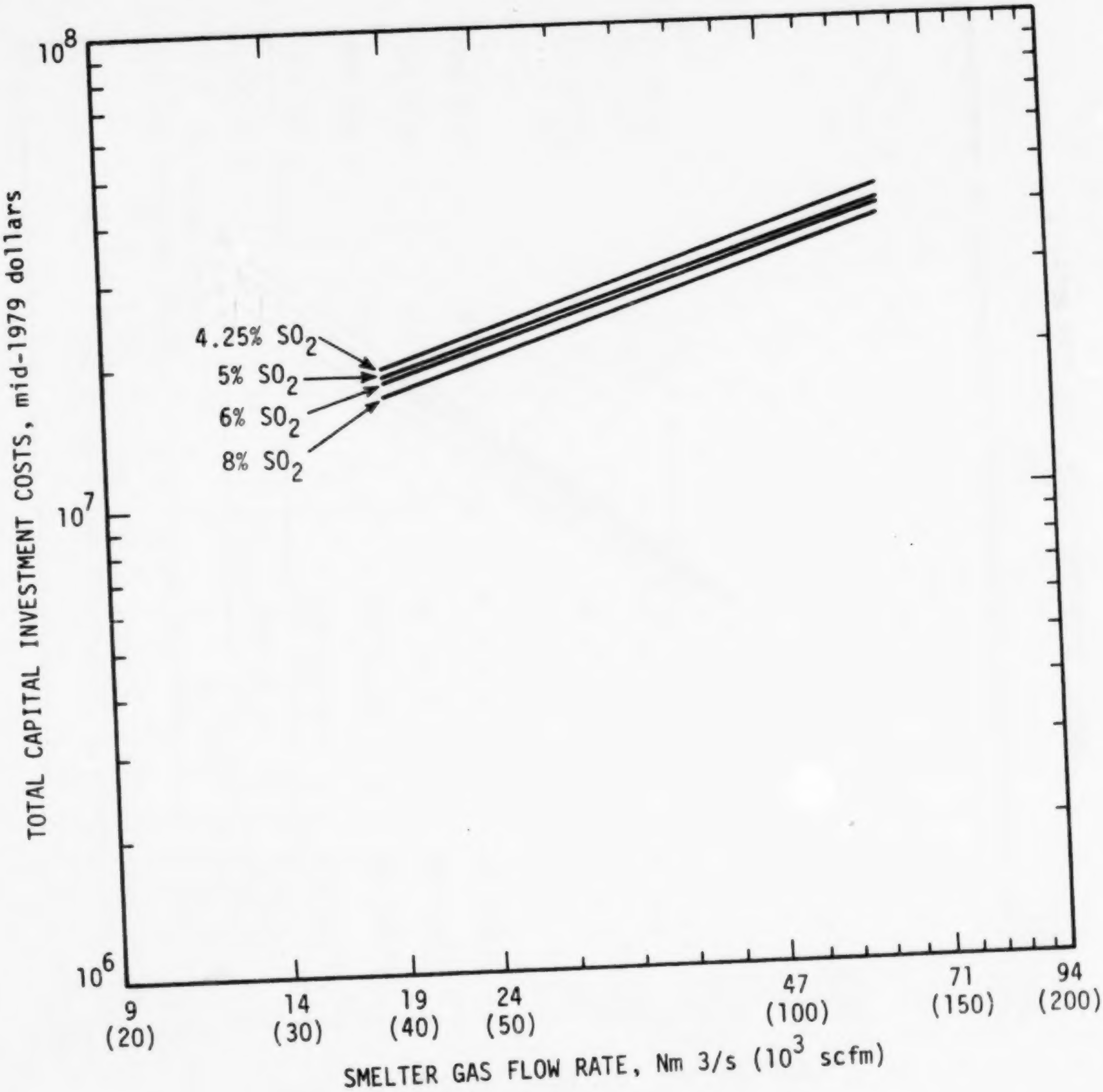

Figure 5.1-3. Total capital investment costs of double-contact sulfuric acid plants - dilute feed gas.[89]

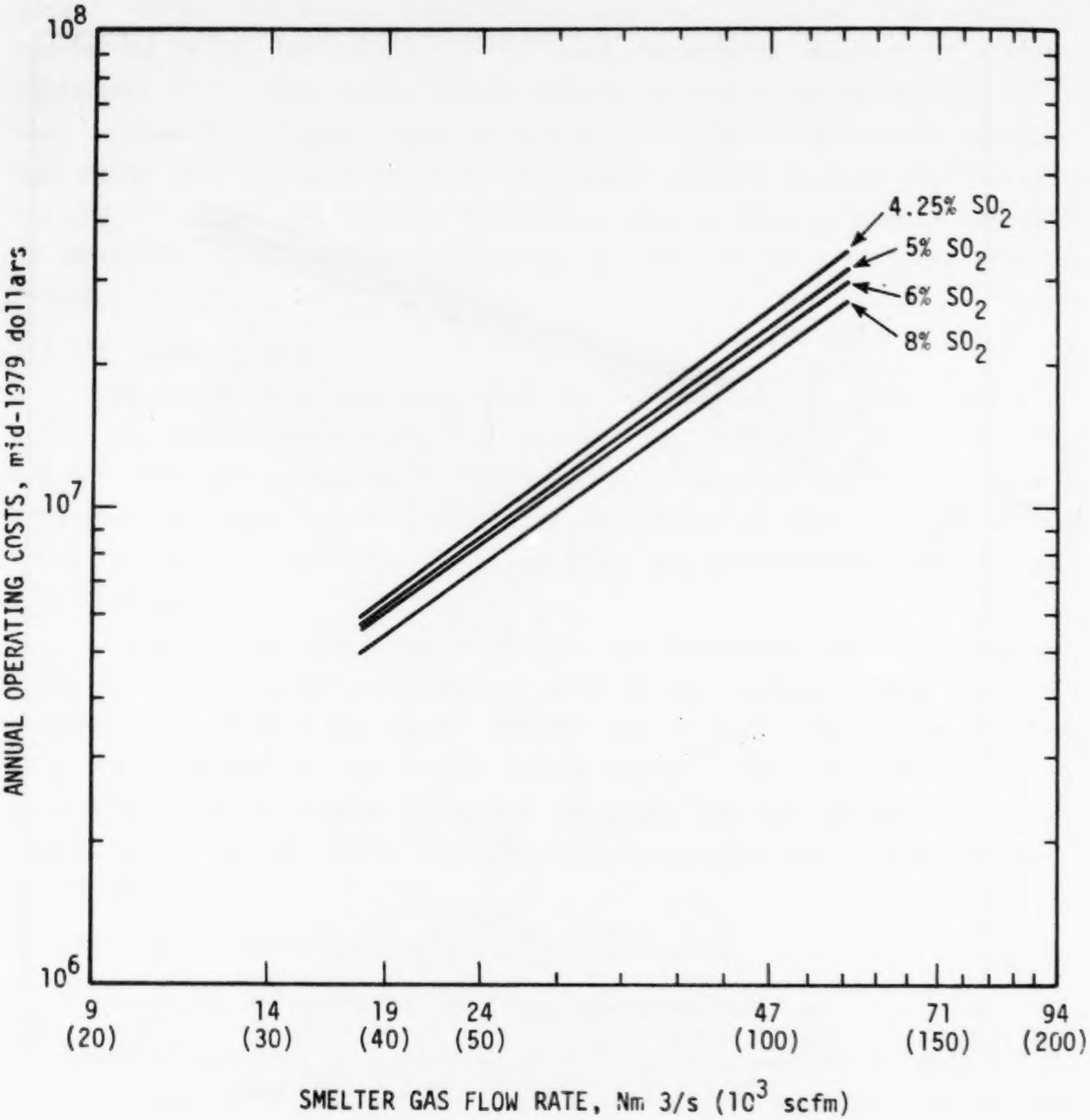

Figure 5.1-4. Annual operating costs of double-contact sulfuric acid plants - dilute feed gas.[89]

TABLE 5.1-3. SUMMARY OF CAPITAL AND ANNUAL COSTS FOR VARIOUS FGD SYSTEMS AT PRIMARY COPPER SMELTERS[a]

FGD system	Capital costs, $		Annual costs, $	
	1% SO_2[b]	1.4% SO_2[c]	1% SO_2[c]	1.4% SO_2[c]
Lime	6,620,700	6,021,800	4,365,600	4,305,400
Limestone	8,518,300	8,132,400	3,667,900	3,553,900
Magnesium oxide	9,897,800	9,156,700	4,059,200	3,874,300
Citrate	4,751,400	4,446,100	1,924,300	1,806,000
Liquid SO_2 system				
Magnesium oxide	1,048,000	1,157,800	935,300	1,007,300
Citrate	878,300	904,100	513,800	524,600

[a] Adapted from EPA.[91]

[b] 98,900 Nm^3 (58,200 scfm).

[c] 76,500 Nm^3 (45,000 scfm).

volume and SO_2 content. The cost estimates shown in Table 5.1-3 are based on an assumption of steady-state operation.

Lead and zinc industries--Most of the SO_2 controls used by lead and zinc industries are directed toward sulfuric acid manufacture. The cost curves presented earlier for sulfuric acid plants are applicable to SO_2 control of lead and zinc smelting operations.

The cost requirements of various SO_2 control alternatives for model lead and zinc smelting facilities were also estimated.[92,93] Estimated capital and annual costs (adjusted to mid-1979) of a DMA scrubbing system and dual-stage sulfuric acid plant with neutralization applicable to conventional sintering machine operations are \$42.7 million and \$11.2 million.[92] The capacity of the DMA scrubbing system is 85,000 Nm^3/h (50,000 scfm) of off-gas. The estimated capital and annual costs (adjusted to mid-1979) of a DMA scrubbing system used in conjunction with a dual-stage sulfuric acid plant and neutralization applicable to roaster/sinter zinc smelting operations are \$50.4 million and \$12.4 million.[93] No DMA scrubbing system is currently in use at any domestic lead or zinc smelter. Details on cost estimates for various control alternatives are available.[92,93]

A recent study has been made to determine the technical feasibility of various alternatives that could be applied to control SO_2 emissions from the lead smelter sinter machine, the lead smelter acid plant, and the zinc smelter acid plant of Bunker Hill Company in Kellogg, Idaho.[78]

Table 5.1-4 provides the estimated capital and operating costs of six different FGD systems [lime/limestone, double-alkali, citrate, ammonium sulfate, zinc oxide, and aluminum sulfate (DOWA)] applicable to various options.[94] Cost information was not available for the Wellman-Lord process. The costs were determined on a preliminary basis from information provided by various FGD system suppliers and designers.[94] Capital costs include fabricated equipment, engineering, and installation. Annual operating costs include both direct costs such as chemical reagents, operating labor, utilities, etc., and indirect costs such as depreciation, taxes, and plant overhead.

5.1.2.3 Environmental and Energy Impacts--

A general discussion is presented here about environmental and energy impacts of SO_2 control techniques applicable to nonferrous primary smelters.

TABLE 5.1-4. ESTIMATED CAPITAL AND ANNUAL OPERATING COSTS OF OPTIONS FOR SO_2 REMOVAL AT BUNKER HILL SMELTER, KELLOGG, IDAHO[94]
($\$ \times 10^6$)

	Option 1[b]	Option 2[b]	Option 3[c]	Option 4[c]
Gas stream	Weak off-gas from the discharge end of the lead smelter sinter machine	Weak off-gas from the discharge end of the sinter machine or strong sinter machine off-gas during shutdown and malfunction of the acid plant	Tail gas from the lead smelter acid plant	Tail gas from the zinc plant acid plant plus a 15% bypass stream of strong gas which is approximately 15% of the total volume exhausted
Flow rate (wet)				
Nm^3/h } normal	47,000	47,000	45,000	94,000
scfm } normal	28,000	28,000	27,000	56,000
Nm^3/h } range	22,000-50,000	22,000-55,000	30,000-54,000	42,000-120,000
scfm } range	13,000-30,000	13,000-33,000	18,000-32,000	25,000-70,000
Temperature, °C(°F)	190 (370)	190(370)-normal 120(250)-upset	60 (140)	90 (200)
SO_2 composition (Vol %, wet)				
normal	0.7	0.7	0.2	1.0
range	0.5-0.9	0.5-6.0	0.1-0.5	0.1-1.5
Gas composition (Vol %, wet)				
CO_2	0-1	0-1	2	0
O_2	20	20	12	8
CO	0-1	0-1	0	0
H_2O	7	7	1-2	7

(continued)

TABLE 5.1-4 (continued)

	Option 1[b]	Option 2[b]	Option 3[c]	Option 4[c]
FGD system costs				
Lime/limestone				
Capital	1.72	Not	1.83	
Annual	1.02		0.65	
Double-alkali		estimated		
Capital	2.58		2.15	
Annual	1.18		0.66	
Citrate				
Capital	3.87		3.55	5.05
Annual	0.76		0.78	0.44
Ammonium sulfate				
Capital	4.19		2.80	7.10
Annual	0.76		0.76	1.51
Zinc oxide				
Capital	4.62		3.98	7.31
Annual	1.29		1.08	2.37
Aluminum sulfate (DOWA)				
Capital	4.73		3.23	9.14
Annual	1.40		0.88	3.12

[a] Costs adjusted to mid-1979, minimum 80 percent SO_2 removal, 80 percent annual operating factor for all options except option 4 (95 percent annual operating factor).

[b] Particulate loading, 1.0-4.6 g/Nm^3 (0.5-2.0 gr/scf).

[c] Particulate loading, <0.2 g/Nm^3 (<0.1 gr/scf).

Environmental impact--For the primary nonferrous smelting industry, two distinct potential sources of secondary pollution can be identified.[94] The first type results from the application of sulfuric acid plants to strong sulfur dioxide smelter off-gases; if the sulfuric acid cannot be marketed, it must be neutralized with the resulting production of a solid waste. The other type is associated with application of scrubbing techniques to weak gas streams, which create wastewater or waste solids. It is anticipated that the production and possible disposal of solid wastes, elemental sulfur, and liquid SO_2 will not produce secondary pollution if adequate safeguards are taken.[95]

Neutralization of abatement-derived sulfuric acid may produce both land pollution and water pollution if a marketable application for the neutralized acid sludge (gypsum) cannot be found. Although no purposeful neutralization is now practiced, some leaching of waste rock dumps is probably intended at least in part to dispose of excess acid. Ponding has been a technique favored by a number of industries for waste disposal of this type of sludge. Procedures and techniques are available that will prevent the water pollution problems of neutralization and subsequent ponding from occurring:

- Proper site selection and location of waste disposal ponds
- The use of impermeable pond liners
- Closed-loop operation of ponds to prevent pond liquor overflow

A "dry" sulfuric acid neutralization process shows promise for producing minimal secondary pollution problems.[95]

The purge or spent scrubber solutions from the ammonia-based, sodium-based, dimethylaniline, and calcium-based scrubbing systems, if directly discharged to a local water course, could produce water pollution. The possible forms of water pollution include chemical oxygen demand, dissolved solids, increased organic content, soluble salt content, and increased water hardness. Methods to solve the problems of water pollution are available and have been demonstrated for both the ammonia- and sodium-based scrubbing systems. Practical disposal methods for the dimethylaniline purge are also available. Closed-loop effluents or water treatment facilities will, in most situations, be required for the spent calcium-based scrubber solution; solid waste pollution is a possible result of this scrubbing technique.[95]

Energy impacts[96]--Large amounts of energy are required in the execution of most conventional metallurgical extraction processes. The production of aluminum, for example, is one of the most energy intensive metallurgical extraction processes and requires energy in the range of 162,900-209,400 kJ/kg (70,000-90,000 Btu/lb) of aluminum.[96] The energy requirements associated with the production of copper, lead, and zinc are considerably less than this, although still significant.

It is possible to compare the energy requirements of new nonferrous smelting technologies having SO_2 emission controls with the energy requirements of conventional domestic nonferrous smelting technology not having emission controls.[96] Because the energy impact depends on the type of smelting used, a more accurate comparison would relate the overall production of a unit of nonferrous metal with and without SO_2 controls.

In copper smelting, the energy effect attributable to SO_2 control of gas from conventional reverberatory furnace smelting would result in an increase from 20,900-34,900 kJ/kg (9,000-15,000 Btu/lb) of copper to 23,300-37,200 kJ/kg (10,000-16,000 Btu/lb) of copper, with or without neutralization of the sulfuric acid produced. This represents an energy increase of 5 to 10 percent.[96]

With regard to zinc and lead smelters, complete SO_2 control would result in an increase of 1 to 5 percent in the energy requirements associated with the production of zinc and an increase of 5 to 10 percent in the energy requirements associated with production of lead.[96] These are increases over the energy requirements for production of zinc and lead by conventional domestic technology without emission controls.

Although double-absorption sulfuric acid plants require about 15 percent more energy to operate than single-absorption sulfuric acid plants, the incremental impact in terms of the increase in the overall energy requirements associated with the production of a unit of copper, zinc, or lead is only about 2 percent. The production of elemental sulfur requires from 4 to 6 times the energy required for the production of sulfuric acid per unit weight of copper or lead, and from 8 to 12 times the energy required for the production of sulfuric acid per unit weight of zinc.[96]

Dimethylaniline scrubbing, for example, requires only about 121 kWh/Mg (110 kWh/ton) of sulfur dioxide recovered when treating off-gases of 5 percent sulfur dioxide.[96] When used to treat off-gas streams similar to those that could be treated by sulfuric acid plants, DMA scrubbing requires about the same amount of energy as a sulfuric acid plant. When DMA is used to treat off-gases with low concentrations of sulfur dioxide, however, the energy requirement per unit of sulfur dioxide recovered increases by as much as an order of magnitude.

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5.2 IRON AND STEEL PRODUCTION

The primary processes at an integrated steelmaking facility are production of coke, reduction of iron ore to pig iron in a blast furnace, and refining of the pig iron into various grades of steel. These processes involve a diversity of operations, as shown in the composite flow diagram, Figure 5.2-1.

In the blast furnace, the combustion of coke provides the reducing atmosphere that converts the iron ore to metallic iron or pig iron. The pig iron is refined into steel by oxidizing the impurities and adjusting the alloy content to specified levels. Refining is done in various types of steelmaking furnaces: open-hearth, basic oxygen, or electric arc furnaces.

Sulfur dioxide emissions come primarily from the sintering process and from combustion of coke-oven gas and fuel oil. Most of the sulfur from the ore and coke combines chemically with other substances in slag from the blast and steelmaking furnaces. As the slag is cooled, some of this sulfur is released as hydrogen sulfide or SO_2. Figure 5.2-2 shows the overall sulfur balance at a small integrated steel plant.[1] The specific sulfur balance will be different for each plant depending upon raw material analyses, fuels used, and the specific processes employed. In general, however, sintering, combustion of coke-oven gas, and heating processes are the primary SO_2 sources, generating about 1.05 kg of SO_2 per megagram (2.1 lb/ton) of ingot product. The SO_2 emissions and available control methods are discussed in the following sections.

Although foundries and ferroalloy furnaces are sometimes located in integrated steel plants, these sources are usually considered apart from the iron and steel industry for purposes of industrial classification. They are discussed in the following sections, however, because the processes are similar. Foundries and ferroalloy furnaces are not major sources of SO_2, and control techniques are not currently applied solely for SO_2 removal.

5.2.1 Process Descriptions and Emission Sources

5.2.1.1 Sintering--

Process description--The sintering process converts iron-bearing fines into an agglomerated product that is suitable for charging to the blast

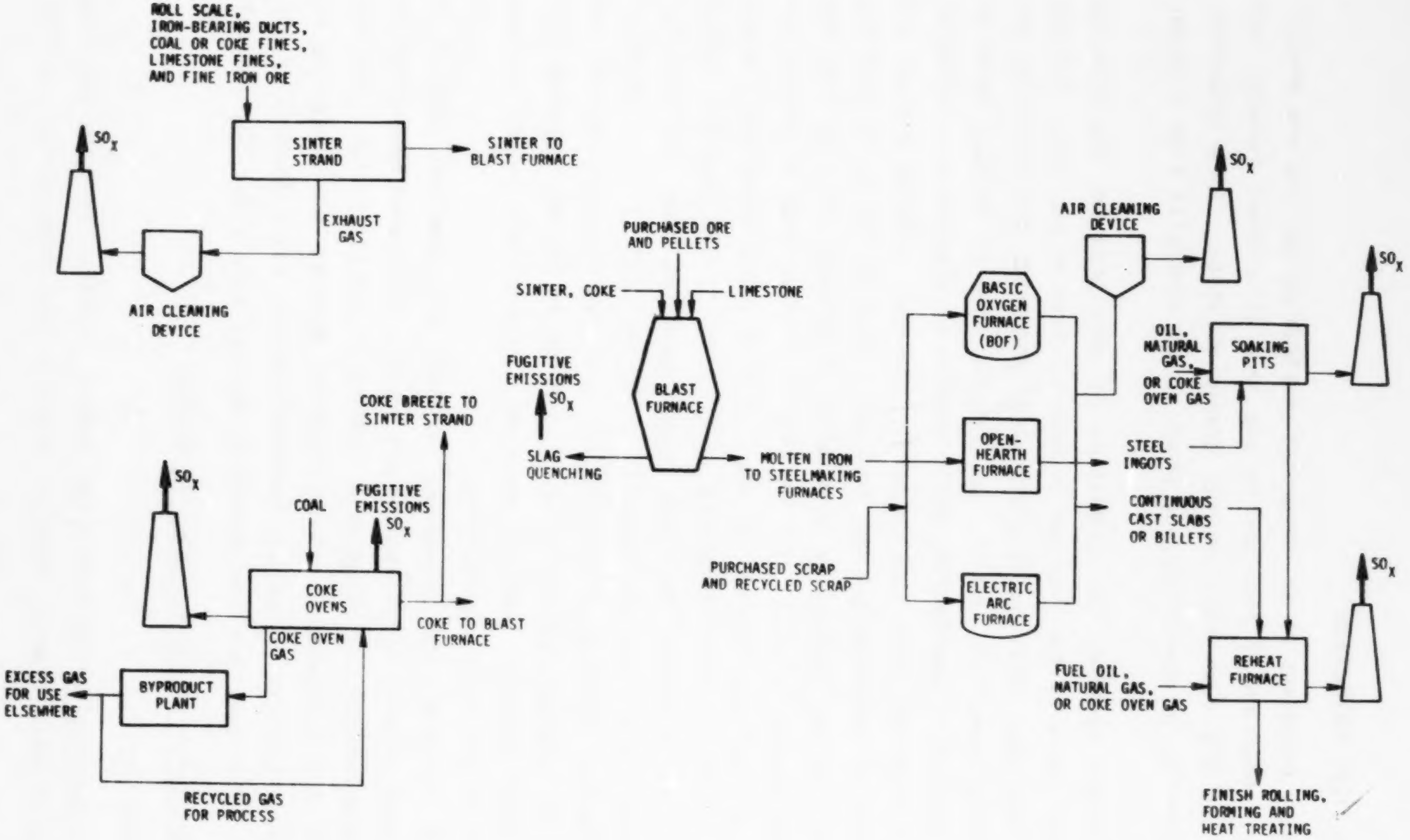
ROLL SCALE, IRON-BEARING DUCTS, COAL OR COKE FINES, LIMESTONE FINES, AND FINE IRON ORE
SINTER STRAND
SINTER TO BLAST FURNACE
EXHAUST GAS
AIR CLEANING DEVICE
SO_X
PURCHASED ORE AND PELLETS
SINTER, COKE
LIMESTONE
BLAST FURNACE
FUGITIVE EMISSIONS SO_X
SLAG QUENCHING
MOLTEN IRON TO STEELMAKING FURNACES
PURCHASED SCRAP AND RECYCLED SCRAP
COKE BREEZE TO SINTER STRAND
COAL
FUGITIVE EMISSIONS SO_X
COKE OVENS
COKE TO BLAST FURNACE
COKE OVEN GAS
SO_X
EXCESS GAS FOR USE ELSEWHERE
BYPRODUCT PLANT
RECYCLED GAS FOR PROCESS
BASIC OXYGEN FURNACE (BOF)
OPEN-HEARTH FURNACE
ELECTRIC ARC FURNACE
AIR CLEANING DEVICE
SO_X
OIL, NATURAL GAS, OR COKE OVEN GAS
SOAKING PITS
SO_X
STEEL INGOTS
CONTINUOUS CAST SLABS OR BILLETS
FUEL OIL, NATURAL GAS, OR COKE OVEN GAS
REHEAT FURNACE
SO_X
FINISH ROLLING, FORMING AND HEAT TREATING

Figure 5.2-1. Simplified flow diagram of an integrated steelmaking facility showing only major sources of sulfur oxide emissions.

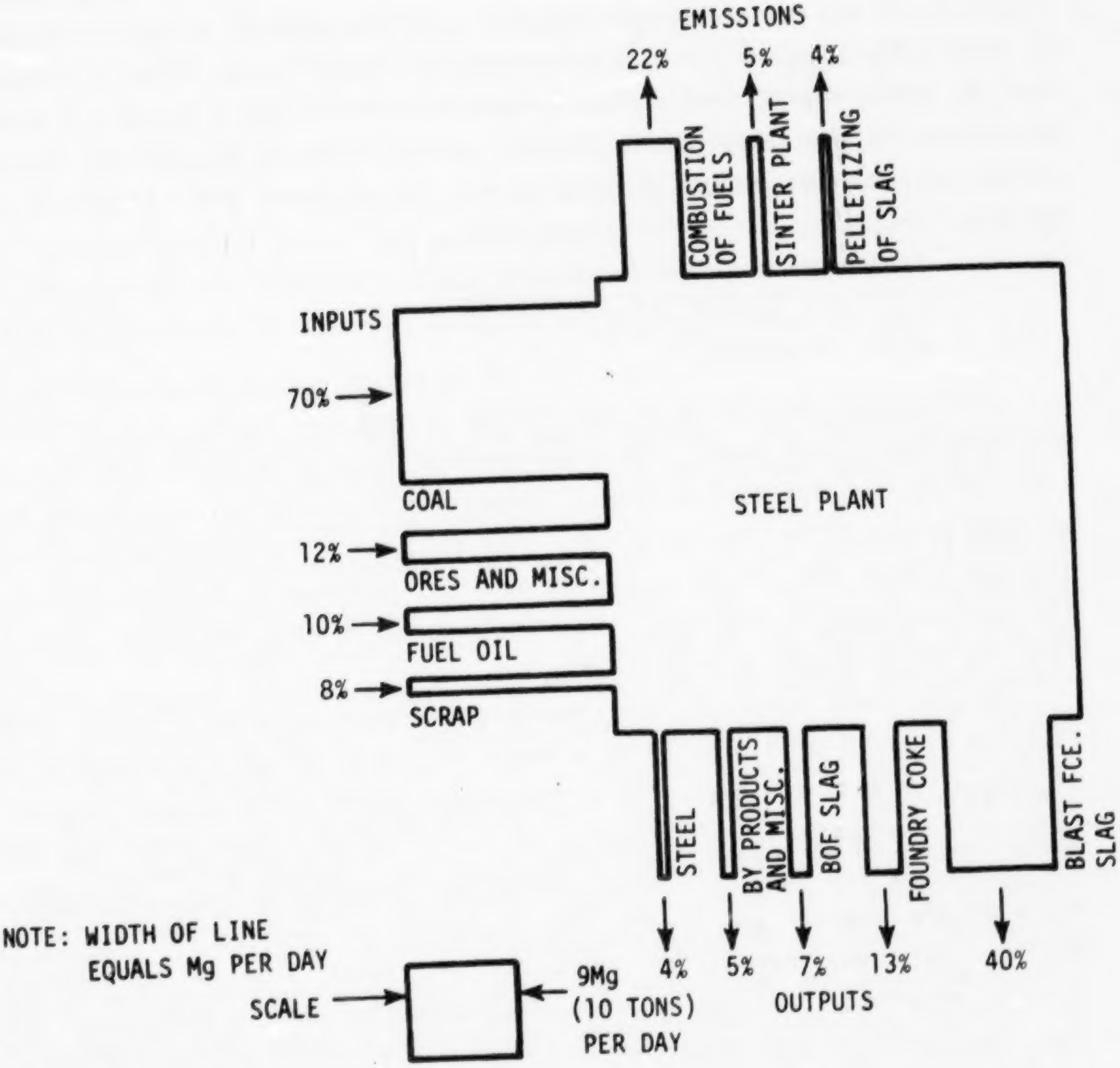
EMISSIONS
22%
5%
4%
COMBUSTION OF FUELS
SINTER PLANT
PELLETIZING OF SLAG
INPUTS
70%
COAL
12%
ORES AND MISC.
10%
FUEL OIL
8%
SCRAP
STEEL PLANT
STEEL
BY PRODUCTS AND MISC.
BOF SLAG
FOUNDRY COKE
BLAST FCE. SLAG
4%
5%
7%
13%
40%
OUTPUTS
NOTE: WIDTH OF LINE EQUALS Mg PER DAY
SCALE
9Mg (10 TONS) PER DAY

Figure 5.2-2. Representation of the overall sulfur balance at one steel plant producing 908 Gg (1 million tons) of ingots annually.[1] (Based on the Alan Wood Plant)

furnace. Iron-bearing fines consist of the dust collected from air pollution control devices, roll scale, and finely crushed iron ore. Particle sizes of these materials range from less than 10 microns to 0.6 cm (0.25 in.), and they cannot be used as blast furnace feed without first agglomerating. The fines are mixed with equally fine limestone or dolomite and coal or coke. Mixtures with a high percentage of limestone or dolomite produce what is called superfluxed sinter. Water is added to the mixture to provide cohesiveness. The proportions of the constituents in the mixture can be varied over a wide range; a typical mix for a superfluxed sinter is as follows:[2]

Iron-bearing fines--70 percent
Limestone or dolomite--18 percent
Coal or coke--4 percent
Water--8 percent

The mixture is placed on the sinter strand (an endless moving grate made from cast steel bars), and a burner hood located near the feed end of the unit ignites the coal or coke. Combustion air is drawn through the bed of material from the top by a fan. The combustion is self-supporting and provides enough heat to cause surface melting, reaction of the constituents, and agglomeration of the mix. The temperature at the combustion zone is 1300° to 1500°C (2400° to 2700°F).[2]

Typical heat input to the combustion furnace is about 174,000 kJ/Mg (150,000 Btu/ton) of sinter.[2] As a means of achieving uniform distribution of combustion air, the underside of the sinter machine incorporates compartments called windboxes. The process fan pulls the air through the bed into the windboxes, and then into a duct to the air cleaning device. The temperature of the exhaust gas in the duct is typically 100° to 150°C (215° to 300°F). Air requirements for sintering are about 3100 Nm^3/Mg (100,000 scf/ton) of sinter produced.[2] For a plant producing 4540 Mg (5000 tons) per day, the discharge gas volume would be about 9,900 Nm^3/min (350,000 scfm).

The sintered cake that falls from the end of the strand is crushed and screened. The undersize portion is recycled to the feed mix, and the remainder is allowed to cool. In 1976 sinter production in the United States was about 32.7 Tg (36 million tons).[3]

Emission sources--The only SO_2 emitted from the sintering process is in the windbox exhaust gases. The amount depends on the sulfur content of the raw materials and the amounts of fuel and limestone used. The sinter product retains as much as 50 percent of the input sulfur.[4,5] The concentration of SO_2 in the exhaust gases ranges from 20 to 398 ppm and averages about 110 ppm, which is equivalent to about 0.9 g/kg (1.8 lb/ton) of sinter.[6] Based on the 1976 industry production of 32.7 Tg (36 million tons),[3] the annual uncontrolled SO_2 emissions from sintering are 29,400 Mg (32,400 tons). For an uncontrolled SO_2 emission rate of 30 g/s (238 lb/h), the maximum ambient 3-hour average concentration of SO_2 at ground level is 21 $\mu g/m^3$, and the maximum 24-hour concentration is 4 $\mu g/m^3$.[7] Height of sinter plant stacks ranges from 46 to 61 m (150 to 200 ft).

5.2.1.2 Byproduct Coking Operations--

Process description--Coke is the solid residue from controlled pyrolysis of coal. Coke consists of carbon, 6 to 10 percent ash, 0.5 to 1.0 percent sulfur, and various trace elements.

In the byproduct coking process, which accounts for over 99 percent of U.S. coke production, coal (usually containing less than 1 percent sulfur and about 30 percent volatile matter) is heated in the absence of air in individual ovens. An individual oven is a narrow refractory channel, typically about 12.3 m (40 ft) long, 3 to 6 m (10 to 20 ft) high, and 0.5 m (20 in.) wide. A single oven holds 11 to 33 Mg (12 to 36 tons) of coal. Usually 40 to 70 ovens are arranged side by side to form a coke-oven battery.

Flues between adjacent ovens are heated to produce the high temperature (1200° to 1370°C or 2200° to 2500°F) needed to drive the volatile matter from the coal. Coal is usually charged through three or four ports in the top of the oven from larry cars, which are wide-gauge vehicles fitted with coal hoppers that traverse the entire length of the battery on rails.[8] In recent years, several other methods have been developed for charging preheated coal. When the coal is preheated before coking, it can be charged to the coke oven through a pipeline (with steam conveyance), through a Redler conveyor and special charging machine, or with a specially designed larry car.[9]

When the oven is fully loaded, the charging ports are covered and sealed for the remainder of the coking cycle, which lasts about 18 hours to produce blast furnace coke and 24 to 36 hours to produce foundry coke. The gases generated during the coking cycle are piped to a byproduct recovery section adjacent to the coke-oven battery, where various byproducts (such as tar, anhydrous ammonia or ammonium sulfate, and light oil) are recovered. After the byproducts are removed from the gas, about 40 percent of the gas is used as fuel to heat the coke ovens. The remainder is used as fuel elsewhere in the plant or is flared.

At the end of the coking cycle, doors at the end of the oven are removed, and the incandescent coke is pushed out of the ovens into a special railroad car. The product is then transported to a quenching station, where it is cooled by deluge water sprays.

Sulfur dioxide emissions--The coke-oven gases produced by the controlled pyrolysis of coal contain reduced sulfur compounds in addition to numerous hydrocarbons. About 25 to 30 percent of the sulfur in the coal is discharged in gaseous form as a constituent of the coke-oven gas. Almost all of this sulfur is present as hydrogen sulfide, with minor amounts of mercaptans. The normal range of hydrogen sulfide concentration is 5.7 to 11 g/m^3 (2.5 to 5.0 gr/scf).[10] The average gas yield is 361 Nm^3/Mg (11,500 ft^3/ton) of coal.[11] At a hydrogen sulfide content of 9 g/m^3 (4.0 gr/scf), the potential emissions, expressed as sulfur dioxide, are 6.1 kg/Mg (12.3 lb/ton) of coal. In 1976, about 69 Tg (76 million tons) of coal was processed in the steel industry. These figures result in a potential annual uncontrolled SO_2 emission of 423,000 Mg (466,000 tons).

Use of the coke-oven gas to heat or underfire the coke ovens or as fuel for other combustion operations results in SO_x emissions unless the hydrogen sulfide is removed. At integrated steel facilities, coke-oven gas provides an average of 70 percent of the total underfiring energy and is the exclusive fuel for most batteries. Among merchant or foundry coke plants, coke-oven gas is used almost exclusively for oven heating. In 1976 the underfiring of coke ovens consumed approximately 32 percent of the total coke-oven gas produced.[11] No data are available on the amount of gas flared, but it is minor because most plants attempt to utilize the energy in coke-oven gas (22,100 kJ/Nm^3 or 550 Btu/ft^3) for useful heating.

Although some plants strip the hydrogen sulfide from the coke-oven gas before burning the gas, this practice is not universal. It is generally done only where the gas is used in operations metallurgically sensitive to sulfur or where state regulations require it, as in Pennsylvania and West Virginia.[10] The stripped hydrogen sulfide may be converted to sulfuric acid or elemental sulfur.

Fugitive emissions occur during oven charging and during the coking cycle. These charging and coking emissions are significant with respect to particulate matter and various organic substances, but not with respect to SO_2, since they total about 681 Mg (750 tons) of SO_2 per year based on the coal usage cited earlier and the emission factors cited in Reference 12.

Sulfur dioxide emissions from coal preheating are insignificant because the sulfur in the coal is not released at the low temperatures involved (200° to 425°C or 400° to 800°F). Either coke-oven gas or natural gas is used as fuel for preheating.[13]

As an example of the impact of plantwide coke-oven gas combustion on ambient SO_2, the maximum contributions to average annual ambient SO_2 levels are 13, 23, and 128 $\mu g/m^3$ from plants emitting 4.0, 9.4, and 36.5 Mg of SO_2 per day (4.4, 10.4, and 40.2 tons/day).[10] The specific stack parameters used to obtain these results are not given in the reference. The exhaust stacks at coke-oven batteries are 61 to 77 m (200 to 250 ft) high. Exhaust gas temperatures from coke-oven combustion stacks range from about 130° to 315°C (270° to 598°F).[14] Flow rates vary from 850 to 1870 Nm^3/min (30,000 to 66,000 ft^3/min) depending upon battery capacity, fuel used, and excess air. The flow rates cited are for batteries processing from 37.5 to 52.5 Mg/h (41 to 58 tons/h) of coal with excess air ranging from 33 to 200 percent.[14] The coke-oven gas is also burned in plant boilers and heating furnaces, both of which have stack heights of 61 to 77 m (200 to 250 ft). The gas flow rates from plant boilers and heating furnaces vary widely depending upon size and fuel used. Exhaust flow rates for soaking pits using gas or oil are about 620 Nm^3/Mg (20,000 scf/ton) of steel heated. The corresponding rates for reheat furnaces are 1270 Nm^3/Mg (41,000 scfm/ton).[15] The exhaust gas flows for a boiler with a capacity rating of 44 MW thermal (150 x 10^6 Btu/h) vary from about 815 Nm^3/min (28,800 scfm) for oil or gas firing to 1126 Nm^3/min (39,800 scfm) for coal firing.[16]

5.2.1.3 Heating Furnaces--

Process description--The heating furnaces in steel plants are referred to as soaking pits, reheat furnaces, heat-treating furnaces, or annealing furnaces, depending upon their metallurgical function. Many of these furnaces are equipped to fire various types of fuel including oil, natural gas, coke-oven gas, and blast furnace gas.

Soaking pits are box-shaped furnaces 6 to 12 m (20 to 40 ft) square and 5 m (15 ft) deep. Steel ingots are placed in the furnace and heated for 12 to 24 hours at about 1300°C (2400°F) to bring them to a uniform temperature for subsequent rolling into slabs, blooms, or billets. Soaking pit furnaces are arranged in groups of 4 to 16 furnaces or more and are fired with natural gas, low-sulfur oil, or coke-oven gas. The sulfur content of the fuel is important metallurgically because certain grades of steel are sensitive to absorption of sulfur. The presence of sulfur may affect the surface quality of the product during subsequent rolling operations. The energy requirement for the soaking pit operation is about 1.16 to 1.74 GJ/Mg (1.0 to 1.5 million Btu/ton).[17-19]

When steel is cast continuously, the ingot and soaking pit operations are eliminated, because the steel is cast directly into the intermediate shapes required for final rolling. Continuous casting has been adopted in most newer plants and so-called minimills because of the energy savings and higher yield.

Reheat furnaces are of various sizes and types, depending on the product being heated. They serve the purpose of reheating intermediate steel shapes to a temperature high enough to permit further rolling or shaping, about 1300°C (2400°F). The energy used for reheating slabs is about 2.9 to 3.5 GJ/Mg (2.5 to 3.0 million Btu/ton). The fuels are natural gas, low-sulfur oil, and coke-oven gas.[20-22]

Heat-treating furnaces, generally operating in the range of 425° to 870°C (800° to 1600°F), are used to impart strength and hardness to the finished product. Heat treating can be a batch or continuous operation. There are numerous variations in the design of heat-treating furnaces but these differences are not significant with respect to emissions. Combustion products are normally vented into the building and escape through roof openings. Heat-treating furnaces generally burn natural gas or residual oil.

An annealing furnace is a special type of heat-treating furnace used to anneal (soften) steel that has been cold-rolled. The annealing furnaces are normally indirect-fired to prevent formation of scale on the steel. A cylindrical cover is placed over the charge, forming a chamber that is filled with a reducing gas to keep products of combustion from contacting the steel. Furnace temperatures for annealing steel range from about 600° to 760°C (1100° to 1400°F). In the annealing of strip steel, the facility consists of 10 to 50 batch furnaces. A continuous annealing furnace can supplant many batch furnaces. It is a tall structure in which the steel strip is looped several times as it travels through the furnace to achieve long exposure time. Combustion products from annealing are usually vented into the building. The energy requirement for annealing is about 0.9 to 1.5 GJ/Mg (0.75 to 1.25 million Btu/ton) of steel.[23-25]

Sulfur dioxide emissions--The SO_2 emissions from heating operations are a function of the fuel used. Table 5.2-1 shows the calculated SO_2 emissions from soaking pits and reheat furnaces burning oil or coke-oven gas.[15] Emissions of SO_2 from annealing furnaces are minor because high-sulfur fuels are seldom burned.

In 1976 the total energy consumed by the steel industry in heating and annealing furnaces was estimated to be 6.1×10^8 GJ (5.77×10^{14} Btu).[26] This consisted of 2.24×10^6 m^3 (592 million gal) of fuel oil, 9.57×10^9 m^3 (335 billion ft^3) of natural gas, 8.14×10^9 m^3 (285 billion ft^3) of coke-oven gas, and 3.49×10^9 m^3 (122 billion ft^3) of blast furnace gas. Calculations based on an average sulfur content of 1.0 percent in fuel oil and an average hydrogen sulfide content of 4.5 g/m^3 (2 gr/ft^3) in coke-oven gas (assuming that about half of the gas is desulfurized) yield the total uncontrolled SO_2 emissions from fuel combustion. The values are 112,500 Mg/yr (124,000 tons/yr), or 0.95 kg/Mg (1.9 lb/ton) of raw steel.

5.2.1.4 Foundries--

Process description--Foundries produce castings for automotive parts, light and heavy machinery, pipe, and a wide range of miscellaneous products.

TABLE 5.2-1. SULFUR DIOXIDE EMISSIONS FROM SOAKING PITS AND REHEAT FURNACES[15]

	Soaking pits	Reheat furnaces
Fuel usage, GJ/Mg (10^6 Btu/ton)	1.57 (1.35)	3.2 (2.8)
SO_2 emissions from firing of oil with 1% S,		
kg/Mg (lb/ton)	0.75 (1.5)	1.5 (3.1)
kg/GJ (lb/10^6 Btu)	0.47 (1.1)	0.47 (1.1)
SO_2 emissions from firing of desulfurized coke-oven gas containing 1 g hydrogen sulfide/m^3 (50 gr hydrogen sulfide/100 ft^3),		
kg/Mg (lb/ton)	0.18 (0.36)	0.38 (0.75)
kg/GJ (lb/10^6 Btu)	0.12 (0.27)	0.12 (0.27)

The process involves melting scrap metal and/or pig iron (crude iron in the form of blocks) and pouring the molten metal into prepared molds. The two major categories of foundry product are "gray iron" and "steel." Both consist mostly of elemental iron, but gray iron contains 2 to 4 percent carbon whereas steel contains 1 percent or less. Gray iron contains various amounts of other elements, generally less than 1 percent. Steel may also contain alloying elements. Such terms as "malleable," "white," and "nodular" iron are used to describe gray iron castings with specific properties.

Figure 5.2-3 illustrates the process flow in a typical gray iron foundry. More than 75 percent of the U.S. installations use a cupola furnace to melt the raw materials, but the use of electric furnaces is increasing.[27,28] In 1973 electric arc furnaces accounted for 17 percent of total gray iron production.[28] Cupola capacities range from 1 to 45 Mg (1 to 50 tons) of melted metal per hour; over 60 percent operate in the range of 2.7 to 9.9 Mg (3 to 11 tons) per hour. Electric induction and reverberatory furnaces are also used in gray iron foundries.

The cupola is a refractory-lined, cylindrical furnace resembling a small blast furnace. Raw materials consisting of iron scrap, pig iron, fluxes, and coke are charged through a door in the top of the cupola. Fluxes are limestone or similar minerals, which absorb or react with impurities after the charge has melted. The coke is burned by blowing air through ports (tuyeres) near the bottom of the furnace. The air may be preheated as high as 980°C (1800°F) to reduce coke consumption.[29] At cupola blowing rates of 142 to 425 Nm^3/min (5,000 to 15,000 scfm) with a preheat temperature of 550°C (1,000°F), the melting rates are 8.2 to 22.7 Mg/h (9 to 25 tons/h).[30] This corresponds to about 1090 Nm^3/Mg (35,000 ft^3/ton); the undiluted exhaust flow rates from cupolas average about 903 Nm^3/Mg (29,000 ft^3/ton).[31] The dilution air introduced from the combustion of carbon monoxide as well as from the charging door is about equal in volume to the undiluted gas flow.[31] As the charge melts, the molten material flows to the bottom of the furnace, from which molten iron is drained periodically or continuously. Additional raw materials are added to keep the furnace full. Operation of the cupola furnace is normally continuous, but it is operated over a much shorter period than a blast furnace because the cupola must be reconditioned about once a week.

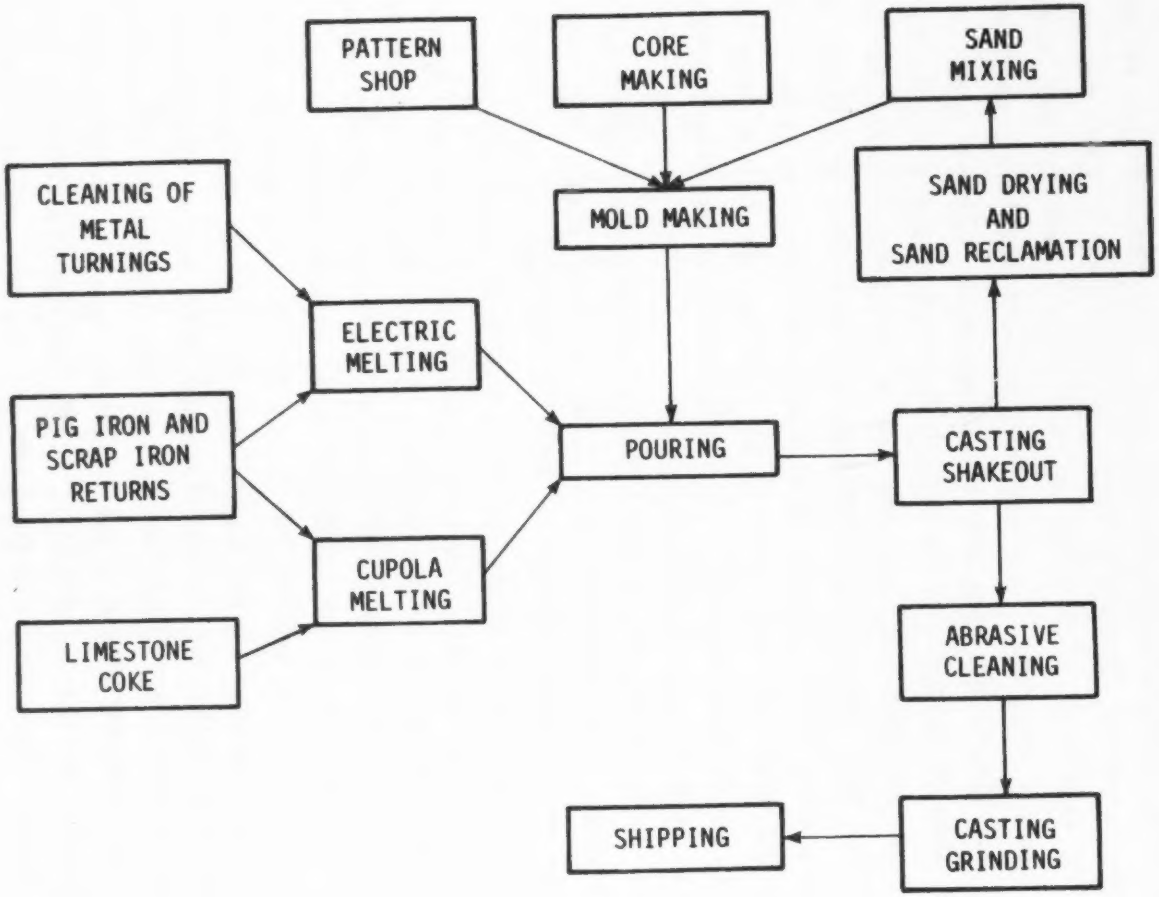
PATTERN SHOP
CORE MAKING
SAND MIXING
CLEANING OF METAL TURNINGS
MOLD MAKING
SAND DRYING AND SAND RECLAMATION
ELECTRIC MELTING
PIG IRON AND SCRAP IRON RETURNS
POURING
CASTING SHAKEOUT
CUPOLA MELTING
LIMESTONE COKE
ABRASIVE CLEANING
SHIPPING
CASTING GRINDING

Figure 5.2-3. Flow diagram of a gray iron foundry.

Where electric arc, electric induction, and reverberatory furnaces are used in gray iron foundries, the charge consists mainly of iron scrap, pig iron, and limestone. These furnaces are operated on a batch basis. The reverberatory furnace is heated by firing gas or oil. The molten metal is drained from the melting furnace at a temperature of about 1600°C (2900°F) into a ladle and then into prepared molds. After solidification the castings are removed from the molds and cleaned by shot blasting.

Castings intended for certain uses may be heat-treated for several hours at temperatures of 530° to 900°C (1000° to 1600°F). Heat-treating furnaces, fired by gas or oil, are referred to by many different names, including "annealing," hardening," "car-bottom," and "traveling hearth." Castings that have been annealed are often referred to as "malleable iron castings."

The cores and molds are formed in the desired shape from sand and binders and are cured either in a baking oven (core oven) at 150° to 260°C (300° to 500°F) or at room temperature. Curing evaporates moisture and hardens the sand mixture. Core ovens are fired with natural gas or oil.

In 1978 the total shipment of gray, ductile, and malleable iron castings was 14.8 Tg (16.3 million tons). Gray iron castings accounted for 77 percent of the total.[32] A 60 percent yield of good castings means total production was about 24.7 Tg (27.2 million tons).

Steel foundries are similar to gray iron foundries; the main difference is that electric furnaces and open hearth furnaces, rather than cupola furnaces, are used for melting. The raw materials consist of steel scrap, pig iron, and fluxes. The open hearth furnaces are fired with gas or oil. Sometimes supplemental oxygen is blown into the open hearth furnace and the arc furnace to accelerate the process, a procedure called oxygen lancing.

Large steel foundries operate 24 hours a day and 7 days a week, whereas smaller ones operate 8 hours a day. Capacities of foundries range from 5 to 216 Mg/day (5 to 240 tons/day).[33] Total shipments of steel castings in 1978 were 1.7 Tg (1.9 million tons).[32]

Sulfur dioxide emissions--Sulfur dioxide emissions from cupolas depend upon the sulfur content of the coke (about 1 percent), the quantity of coke burned, and type of iron being produced. Over 70 percent of the input sulfur is normally contained in the slag and the iron.[34]

At a coke sulfur content of 0.8 percent, and a metal-to-coke ratio of 9 to 1, the SO_2 emission rate estimated by one source is 0.18 kg/Mg (0.36 lb/ton) of metal charged, equivalent to about 57 ppm in the cupola off-gas.[34] Another source reports SO_2 concentrations of 25 to 250 ppm in the cupola off-gas.[35] Based on the emission value of 0.18 kg/Mg (0.36 lb/ton) and the 1973 production of 20.5 Tg (22.6 million tons) of iron, the annual uncontrolled SO_2 emissions from cupolas are 3700 Mg (4000 tons). Cupolas are not generally considered a significant source of SO_2 emissions because of the inherent metallurgical restriction on coke sulfur content, i.e., less than 1 percent.[34]

The SO_2 emissions from electric arc furnaces producing gray iron average 0.12 kg/Mg (0.24 lb/ton) of iron.[36] The emissions are highly variable, however, depending on the sulfur content of the scrap and the grade of iron being produced. Total annual uncontrolled emissions of SO_2, based on 1973 production of 4.61 Tg (5.1 million tons), are 545 Mg (600 tons).

The SO_2 emissions from open hearth furnaces are a function of the sulfur content of the fuel and grade of steel being produced. The heat required for 100 percent scrap charges is 1.16 to 1.74 GJ/Mg (1.0 to 1.5 million Btu/ton) of steel.[37] If this heat is supplied by burning of high-sulfur oil, the SO_2 emissions may approach 1.0 kg/Mg (2 lb/ton). Because open hearths are not widely used and the sulfur content of oil is restricted in most localities, SO_2 emissions from open-hearth furnaces are not controlled by add-on control devices.

5.2.1.5 Ferroalloy Production--

Process description--Ferroalloy is the generic term for solid solutions of iron and one or more other elements. Ferroalloys are used in steelmaking as both deoxidizing elements and as alloying constituents. The United States is the world's largest producer and user of ferroalloys.[38] The ferroalloy most widely used in steelmaking is ferromanganese, followed by ferrosilicon, ferrochromium, and ferrophosphorus. Silicomanganese is also considered as a ferroalloy product although it does not contain much iron. The alloys are used in steel manufacturing for deoxidation and to impart special properties to the product metal.

Silicon metal and silicomanganese are not strictly ferroalloys because they contain no iron. They are discussed here because they are manufactured in the same way as ferroalloys, which are made in open-semisealed, or sealed electric submerged-arc furnaces. Ferromanganese is also made in blast furnaces.

The raw materials for ferrosilicon production are iron ore or iron scrap, a silicon ore such as silica sand, coke or coal, and limestone. Production of silicon metal requires silica and coal or coke; production of silicomanganese requires silicon ores, manganese ores, and coal or coke.

The raw materials are charged to the furnace, which is a refractory-lined crucible, and carbon electrodes are immersed in the mix. The mix is melted by resistance heating, i.e., resistance of the charge material to the flow of current between the electrodes. Additional heat comes from chemical reduction of the iron, manganese, and silicon oxides and from oxidation of the coke or coal. The temperature near the electrode tips is estimated to be 2200° to 2760°C (4000° to 5000°F).[39] Impurities rise as a floating slag, and the molten alloy and slag are drained periodically from tapholes near the bottom of the furnace. Once started, the process is essentially continuous. Some 24 ferroalloy plants in the United States produce about 1.5 Tg (1.7 million tons) per year.[40]

Sulfur dioxide emissions--Measured SO_2 emissions from several ferroalloy furnaces have ranged from less than 1 ppm to 17 ppm. The SO_2 emissions from furnaces equipped with control devices did not exceed 3.2 kg/h (7 lb/h).[39]

5.2.1.6 Blast Furnace Slag--

Process description--Sulfur is introduced into the blast furnace primarily through the sulfur in the coke. Because of the reducing conditions and slag composition, most of the sulfur is discharged in the slag. The remainder is dissolved in the molten metal. The blast furnace produces 250 to 400 kg (500 to 800 lb) of slag per megagram (ton) of metal. Sulfur content of the slag is 1.2 to 2.0 percent. Slag is usually discharged from the furnace every 3 to 6 hours; in some of the new, larger furnace operations, the slag is drained continuously. The slag may be drained into a pit and sprayed with water for cooling or may be granulated by introducing water directly into the stream of molten slag on a rotary drum or by application of a fine water spray. When the slag stream contacts water, some of the sulfur is released as fugitive hydrogen sulfide. The quantity depends upon many variables, including the initial sulfur content of the slag and the method of spraying.[41-43]

Sulfur dioxide emissions--The amount of SO_2 released directly from slag pouring is not known. Within the industry there are many variations in slag volume, sulfur content, and pouring and cooling methods. Most of the sulfur released apparently occurs as hydrogen sulfide. Given a slag production estimate of 300 kg/Mg (600 lb/ton) of hot metal, the 1976 production of 79 Tg/Mg (87 million tons) of hot metal,[44] and a slag sulfur loss of 0.24 percent,[41] the potential annual hydrogen sulfide emissions would be 106 Gg (118,000 tons).

5.2.2 Control Techniques

5.2.2.1 Description--

Sintering--Sulfur dioxide emissions from the sinter plant windbox exhaust can be reduced by reducing the total sulfur input from the raw materials and by increasing the quantity of limestone feed.[1] These methods may not be feasible, however, because of constraints on the availability of raw materials or metallurgical constraints on product quality. Increasing limestone feed also increases the resistivity of the windbox dust, which decreases particulate removal efficiency for plants using electrostatic precipitators.[45]

Wet scrubbers used for particulate control can also remove as much as 99 percent of the SO_2 when supplemented by injection of caustics.[46] One scrubber removed about 60 percent of the SO_2 when using regular plant water.[46] No wet scrubber systems are installed in the United States for the express purpose of SO_2 control of sinter exhaust. The common element of all SO_2 control systems discussed in the literature is absorption by use of a separate liquid system or a wet scrubber. Four processes have been used in Japan at plants having SO_2 concentrations of 400 to 800 ppm; ammonia is the scrubbing reagent in one process, and lime-limestone in the other three. Reported removal efficiencies range from 90 to 95 percent. In all cases, the SO_2 scrubbing systems follow particulate collection using an electrostatic precipitator. The flow rates at the 12 plants using these systems range from 2,000 to 33,000 Nm^3/min (71,000 to 1,200,000 ft^3/min).[46]

Byproduct coking operations--Several processes are suitable for removing hydrogen sulfide from coke-oven gases. These processes either recover elemental sulfur or produce a concentrated stream of hydrogen sulfide, which in turn can be converted into sulfuric acid or elemental sulfur. The processes most commonly used to produce sulfur are the Stretford, Takahax, Fumaks, and Giammarco-Vetrocoke processes.[47,48] Those producing concentrated hydrogen sulfide are the Vacuum Carbonate, Sulfiban, Dravo/Still, and Diamox processes.[47,48] The Vacuum Carbonate and Sulfiban processes are the most widely used processes in the United States.[49]

In the Vacuum Carbonate process, hydrogen sulfide is absorbed into a 3.0 to 3.5 percent solution of sodium carbonate. The hydrogen sulfide is then stripped by steam from the absorbent in a reactivating tower. The reactivation is performed under vacuum to reduce the quantity of steam required. The hydrogen sulfide content of the coke-oven gas can be reduced by approximately 93 to 98 percent using a relatively new two-stage process. Conventional systems achieve about 90 percent removal.[47,50]

After the stream is condensed, the hydrogen sulfide is available for further use. Of the eight plants using the Vacuum Carbonate system in the United States in 1978, six had Claus sulfur recovery systems.[49] The sulfur recovery plants used in conjunction with the Vacuum Carbonate system typically operate at 95 to 97 percent efficiency. Thus overall hydrogen sulfide removal efficiency using the two-stage Vacuum Carbonate system with sulfur recovery is about 90 to 95 percent.

The Sulfiban process can reduce hydrogen sulfide concentrations in coke-oven gas to less than 0.23 g/m^3 (0.10 gr/100 ft^3) by use of a monoethanolamine (MEA) scrubbing solution. This process also produces a concentrated hydrogen sulfide stream. Three plants planned in the United States as of 1975 all used a Claus plant to recover sulfur from the H_2S stream.[49]

In the Stretford process, the gas is scrubbed in packed towers by an alkaline solution of anthraquinone disulfonic acid (ADA), sodium ammonium vanadate, and buffering compounds. The hydrogen sulfide reacts with the alkali to form sodium hydrosulfide (NaHS). In holding tanks at the bottom of the towers, the NaHS reacts with the vanadium to form free sulfur. The vanadium, which is reduced in the reaction, is reoxidized by the ADA. In subsequent steps the ADA is oxidized, and the sulfur recovered in the molten state. Hydrogen sulfide removal efficiencies can exceed 99 percent.[47,51] This process is currently being used at the Hamilton, Ontario, coke-oven plant of Dominion Foundries and Steel, Limited, and at several plants in Europe.[52,53]

The Takahax and Fumaks processes are similar in configuration to the Stretford process, although the process chemistry differs significantly. These processes are used in Japan with reported hydrogen sulfide removal efficiencies of more than 99 percent.[47,51] These processes all pose a potentially serious water pollution problem if the thiosulfate and thiocyanate are not removed from the wastewater before it is discharged.

Coke-oven gas can come into direct contact with water in various byproduct operations, such as direct-contact coolers. Some hydrogen sulfide is removed, but that which is dissolved in the water is released to the atmosphere if the water is cooled in open cooling towers.

Heating furnaces--The only control for SO_2 from heating furnaces is the choice of fuel. Natural gas and blast furnace gas are essentially free of sulfur. Coke-oven gas that is burned for heating may be either desulfurized or blended with natural gas to dilute the hydrogen sulfide content. Most state regulations limit the sulfur content of oil to 0.5 to 1.0 percent.

Foundries and ferroalloy production--There are no controls for SO_2 emissions from the cupolas, electric arc furnaces, or open-hearth furnaces now in use. Where wet scrubbers are used for particulate control, addition of caustic to the scrubber wastewater can remove significant amounts of SO_2 from the gas.[54]

Blast furnace slag--A variety of operating practices and granulation techniques have been studied to minimize emissions.[41,42] Addition of oxidizing agents to the quench water is effective in reducing hydrogen sulfide emissions but may create higher SO_2 emissions. Reducing the sulfur content of the initial slag to 1.0 to 1.5 percent is effective but is not always feasible for metallurgical reasons.

5.2.2.2 Control Cost--

All costs in this section are referenced to July 1979 dollars. Values obtained from various references were adjusted to July 1979 by use of the Chemical Engineering plant cost index for July 1978 of 220 and an inflation rate of 7.5 percent for the period July 1978 to July 1979.

Sintering--The estimated cost of an installed limestone scrubbing system on a large sinter plant producing 6312 Mg/day (6950 tons/day) with a flow rate of 675,000 Nm^3/h (394,000 scfm) is \$11,900,000. Total annual operating cost including plant and payroll overhead and capital charges is \$4,221,000 or \$2.29/Mg (\$2.08/ton).[55] These costs include a venturi scrubber to remove particulate matter, an SO_2 absorber, limestone preparation equipment, and a water treatment system. Figure 5.2-4 illustrates the components of the system. Tables 5.2-2 and 5.2-3 present the capital and annual operating costs, respectively.

Several sinter plants have been retrofitted for particulate control. Although no U.S. plants have required direct SO_2 control, retrofit of a limestone scrubbing system would be possible where space is available; many steel mills are very congested and might not be able to accommodate limestone and sludge handling facilities.

Byproduct coking operations--Massey and Dunlap have presented costs for various desulfurization processes and associated hydrogen cyanide pretreatment.[56] These costs, adjusted to July 1979 dollars, are summarized in Table 5.2-4.

5.2.2.3 Energy and Environmental Impact--

Sintering--The energy requirements for the limestone scrubbing system described earlier are 12.6 kWh of electricity and 48.6 kg of steam per megagram of sinter (11.4 kWh and 97 lb per ton of sinter).[55] For a plant producing 302,000 Mg (333,000 tons) per year, the energy requirement for a system incorporating an ESP and limestone scrubber is 19.8 kWh/Mg (18 kWh/ton).[57] The limestone scrubbing system generates large quantities of wastewater, which must be treated; treatment in turn produces a sludge that must be disposed of. The limestone scrubbing system requires about 160 liters of water per megagram of sinter (38 gal/ton) and 10 kg of limestone per megagram of sinter (19 lb/ton).

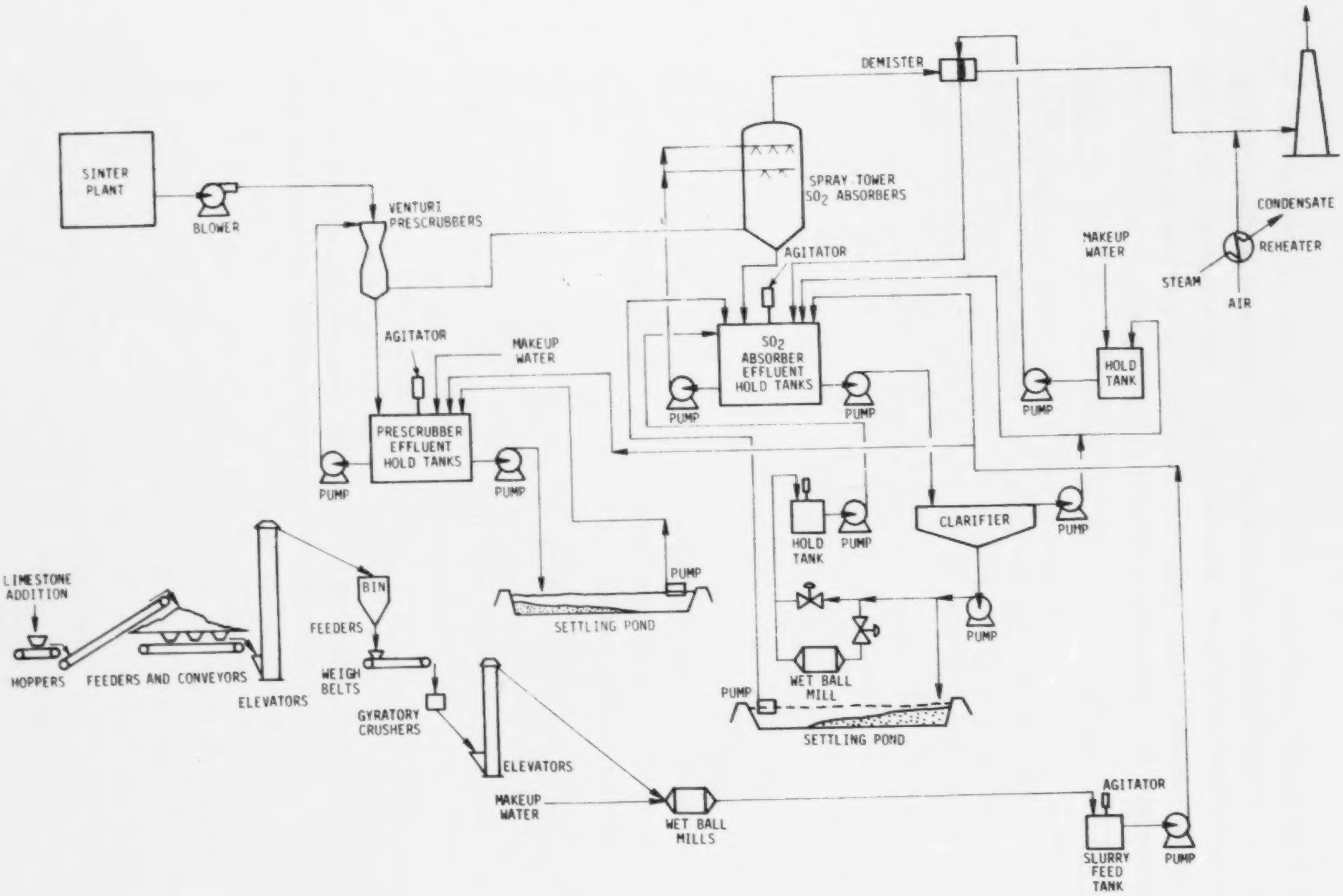
SINTER PLANT
BLOWER
VENTURI PRESCRUBBERS
SPRAY TOWER SO_2 ABSORBERS
DEMISTER
CONDENSATE
REHEATER
STEAM
AIR
MAKEUP WATER
HOLD TANK
PUMP
AGITATOR
SO_2 ABSORBER EFFLUENT HOLD TANKS
PUMP
PUMP
AGITATOR
MAKEUP WATER
PRESCRUBBER EFFLUENT HOLD TANKS
PUMP
PUMP
PUMP
SETTLING POND
HOLD TANK
PUMP
CLARIFIER
PUMP
PUMP
WET BALL MILL
PUMP
SETTLING POND
LIMESTONE ADDITION
HOPPERS
FEEDERS AND CONVEYORS
ELEVATORS
BIN
FEEDERS
WEIGH BELTS
GYRATORY CRUSHERS
ELEVATORS
MAKEUP WATER
WET BALL MILLS
AGITATOR
SLURRY FEED TANK
PUMP

Figure 5.2-4. Limestone scrubbing process for steel mill sinter plant application.[55]

TABLE 5.2-2. CAPITAL COST OF LIMESTONE SCRUBBING SYSTEM ON AN EXISTING SINTER PLANT PRODUCING 6312 Mg/day (5731 tons/day)[55] (mid-1979 dollars)

	Case A, standard operation		Case B, 39% gas recirculation	
Direct costs:[a]				
Process equipment				
Materials handling	38,100		42,000	
Feed preparation	109,000		112,700	
Particulate scrubbing	780,200		624,900	
SO_2 scrubbing	1,190,100		779,500	
Gas reheating	243,900		177,200	
Gas handling	166,100		119,200	
Solids disposal	206,500		222,300	
Services	149,000		149,000	
Particle recirculation	37,000		37,000	
Subtotal		2,920,000		2,264,000
Equipment installation		1,134,000		883,000
Piping		869,000		679,000
Structural steel		145,000		116,000
Foundations		1,751,000		1,358,000
Insulation and painting		58,000		46,000
Electrical		204,000		159,000
Instruments		116,000		90,000
Building and service		146,000		114,000
Excavation and fill site Preparation		290,000		226,000
Sludge ponds (installed)		29,000		23,000
Particulate disposal		139,000		121,000
Calcium solids disposal		197,000		192,000
Subtotal direct costs		7,998,000		6,271,000
Indirect costs:[a]				
Engineering design and supervision		1,042,000		825,000
Construction field expense		1,107,000		876,000
Contractor fees		586,000		464,000
Contingency		1,172,000		927,000
Subtotal indirect costs		3,907,000		3,092,000
Total capital cost		11,905,000		9,363,000

[a] Mid-1977 costs from original reference have been updated to mid-1979 with an inflation factor of 1.159.

TABLE 5.2-3. TOTAL ANNUAL OPERATING COST OF LIMESTONE SCRUBBING ON AN EXISTING SINTER PLANT PRODUCING 6312 Mg/day (5731 tons/day)[55]

	Case A, standard operation	Case B, 39% gas recirculation
Materials and utilities:		
Limestone required, Mg (tons)	17.4×10^3 (19.2×10^3)	17.0×10^3 (18.7×10^3)
Operational labor and supervision man-hours	18,000	18,000
Steam required, Mg (tons)	89,500 (98,600)	44,900 (49,500)
Process water, liters (gal)	290×10^6 (76.7×10^6)	267×10^6 (70.6×10^6)
Electricity, kWh	23.27×10^6	16.80×10^6
Direct costs, $:		
Limestone	123,100	120,600
Operating labor and supervision	193,500	193,500
Steam	318,200	159,600
Water	9,000	8,400
Electricity	700,500	505,700
Maintenance	667,600	523,500
Analytical services	31,600	31,600
Indirect costs, $:		
Capital charges at 14.9% of total investment	1,774,000	1,395,000
Plant overhead at 20% of indirect costs less raw materials	384,100	284,400
Administrative overhead at 10% of operating labor	19,400	19,400
Total annual operating cost	4,221,000	3,242,000

Basis:

Remaining life of sinter plant, 30 yr
Stack gas reheat to 79.4°C (175°F)
Sinter unit on stream 7000 h/yr
Midwest plant location, 1979 operating costs based on 7.5% inflation applied to 1978 operating costs in original reference
Total capital investment: Case A--$11,905,000; Case B--$9,363,000

TABLE 5.2-4. ESTIMATED CAPITAL AND OPERATING COSTS OF COKE-OVEN GAS DESULFURIZATION SYSTEMS[56]

	Vacuum Carbonate[a]				Sulfiban[a]				Stretford[b]
Gas volume, Nm^3/day (scf/day)	0.57×10^6 (20×10^6)		1.7×10^6 (60×10^6)		0.57×10^6 (20×10^6)		1.7×10^6 (60×10^6)		1.7×10^6 (60×10^6)
Control efficiency, %	90	93	90	93	90	98	90	98	99
Capital cost, million $	2.92	2.99	5.03	5.35	3.09	3.32	5.27	5.73	5.27
Operating cost, $/day	1250	1330	3050	3820	1070	1470	2140	3290	2470
Total annualized cost ¢/dam^3 (¢/10^3 scf)	3.5 (9.9)	3.6 (10.2)	2.6 (7.3)	3.1 (8.7)	3.3 (9.3)	4.1 (11.6)	2.1 (6.0)	2.9 (8.3)	2.3 (6.4)

[a] Includes Claus sulfur recovery and hydrogen cyanide pretreatment by catalytic decomposition. Costs based on inlet concentration of 11.4 g/m^3 (5 gr/scf) of hydrogen sulfide with no credit for sulfur recovery.

[b] Includes Woodall Duckham effluent combustion system and no polysulfide pretreatment equipment.

Byproduct coking--The energy requirements for the three desulfurization processes described earlier are presented in Table 5.2-5. The major environmental impact of the wet-oxidative processes (such as the Stretford process) is generation of wastewater containing cyanides, sulfides, and ammonia. For a plant producing 1.7 million Nm^3/day (60 million ft^3/day) of gas, the effluent rate is 32,500 liters/day (8600 gal/day).[51] The Vacuum Carbonate and Sulfiban processes also generate significant quantities of highly contaminated wastewater.

TABLE 5.2-5. NET ENERGY REQUIREMENTS FOR COKE-OVEN GAS DESULFURIZATION PROCESSES[51]

Process	Efficiency, %	Equivalent net energy required, GJ/day (10^6 Btu/day)[a]
Vacuum Carbonate	90	601 (569)
Vacuum Carbonate	93	618 (585)
Sulfiban	90	461 (437)
Sulfiban	98	879 (832)
Stretford[b]	99	210 (199)
Stretford[c]	99	527 (499)

[a] Assume 2556 kJ/kg (1100 Btu/lb) steam, 35% efficiency.

[b] Without pretreatment or effluent treatment.

[c] With effluent treatment.

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5.3 PETROLEUM REFINERIES

Petroleum refineries convert crude oils, various intermediate petroleum fractions, and light gases into useful products. These components are refined by various physical, thermal, catalytic, and chemical processes into liquified petroleum gas (LPG), gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, waxes, tars, asphalts, coke, and petrochemical feedstocks. Most refinery products are not pure chemical compounds but are mixtures of compounds. Some refineries also manufacture pure petrochemicals such as benzene, toluene, and cyclohexane.

Because each refinery is designed to process specific crude oils, no refinery is typical. Most U.S. refineries, however, are designed to maximize production of gasoline. The following are basic operations in refining of crude oil: 1) separation processes, which separate the crude oils to isolate the desired products (e.g., distillation); 2) decomposition processes, which break large molecular chains into smaller ones by cracking (e.g., catalytic cracking, coking); 3) formation processes, which build the products by chemical reaction (e.g., reforming, alkylation, isomerization); 4) treating processes, which remove impurities or compounds that make the products environmentally unacceptable or are detrimental to operation of the refinery; 5) recovery operations (e.g., sulfur recovery, fuel gas recovery); 6) storage; and 7) auxiliary facilities. Figure 5.3-1 depicts a typical petroleum refinery.[1] Because of the complexity of the various processes and the individuality of each refinery, intermediate storage may be needed for certain fractions that will later undergo further processing.

As of January 1979 there were 303 operating petroleum refineries in the United States with total refining capacity estimated to be 3.0×10^9 liters [18 million barrels (bbl)] per calendar day.[2] In some urban areas of the United States there are several refineries with a combined crude processing rate of over 1.6×10^8 liters per day (1 million bbl/day). Refinery processing during 1977 resulted in sulfur dioxide (SO_2) emissions estimated at 800,000 Mg (880,000 tons), or approximately 2.9 percent of total SO_2 emissions in the United States.[3]

In some areas considerable effort has been made to control SO_2 emissions, and many modern refineries have, of necessity, integrated air pollution control into the plant operations.

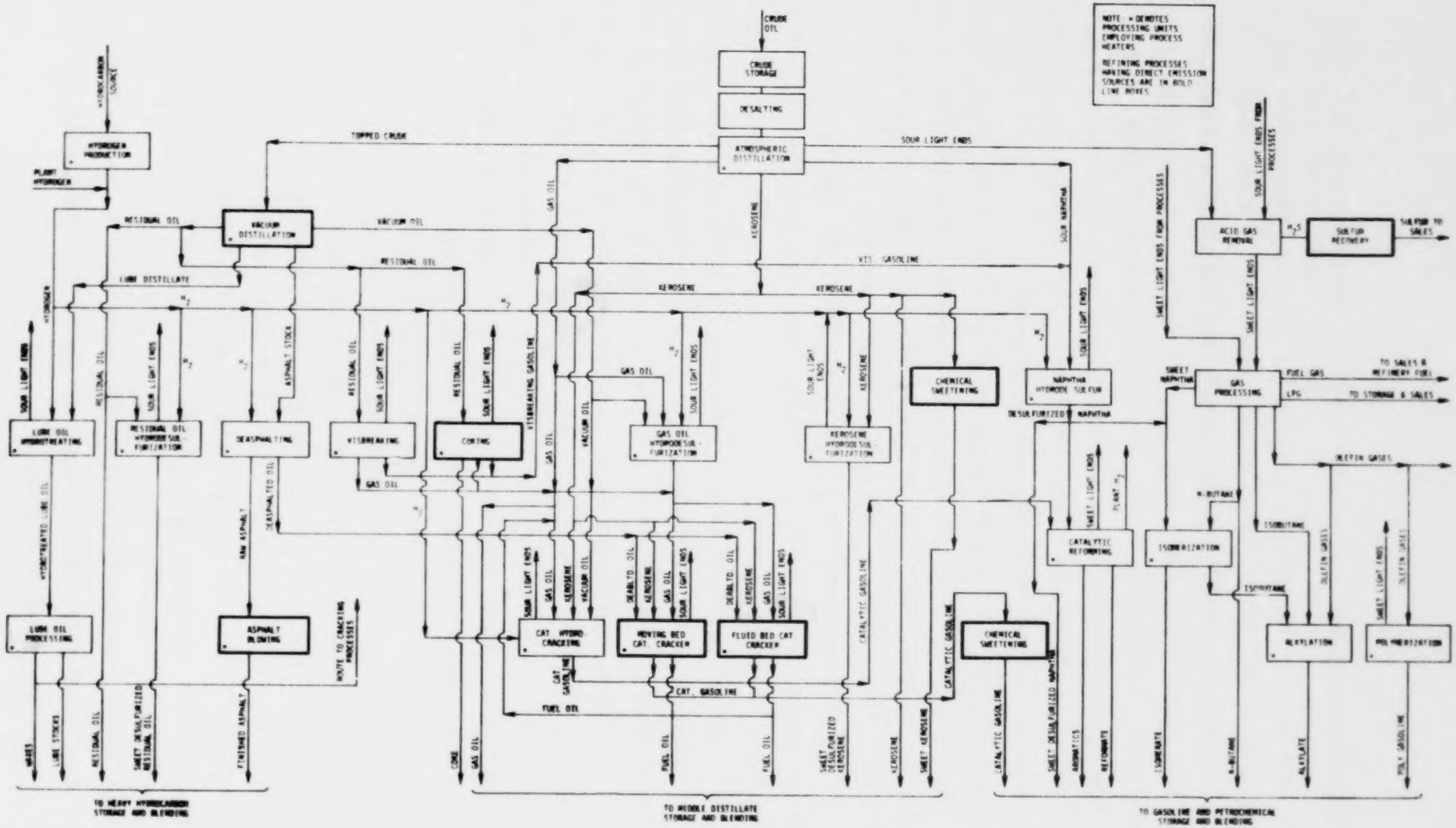

CRUDE OIL
CRUDE STORAGE
DESALTING
ATMOSPHERIC DISTILLATION
NOTE: • DENOTES PROCESSING UNITS EMPLOYING PROCESS HEATERS
REFINING PROCESSES HAVING DIRECT EMISSION SOURCES ARE IN BOLD LINE BOXES
HYDROCARBON SOURCE
HYDROGEN PRODUCTION
PLANT HYDROGEN
TOPPED CRUDE
SOUR LIGHT ENDS
SOUR LIGHT ENDS FROM PROCESSES
SWEET LIGHT ENDS FROM PROCESSES
ACID GAS REMOVAL
H_2S
SULFUR RECOVERY
SULFUR TO SALES
SWEET LIGHT ENDS
VACUUM DISTILLATION
RESIDUAL OIL
VACUUM OIL
GAS OIL
KEROSENE
SOUR NAPHTHA
VIS. GASOLINE
LUBE DISTILLATE
HYDROGEN
H_2
ASPHALT STOCK
VISBREAKING GASOLINE
LUBE OIL HYDROTREATING
RESIDUAL OIL HYDRODESULFURIZATION
DEASPHALTING
VISBREAKING
COKING
GAS OIL HYDRODESULFURIZATION
KEROSENE HYDRODESULFURIZATION
CHEMICAL SWEETENING
NAPHTHA HYDRODE SULFUR
SWEET NAPHTHA
GAS PROCESSING
FUEL GAS
TO SALES & REFINERY FUEL
LPG
TO STORAGE & SALES
DESULFURIZED NAPHTHA
OLEFIN GASES
N-BUTANE
ISOBUTANE
PLANT H_2
HYDROTREATED LUBE OIL
RAW ASPHALT
DEASPHALTED OIL
ROUTE TO CRACKING PROCESSES
DEASLTD. OIL
CATALYTIC GASOLINE
LUBE OIL PROCESSING
ASPHALT BLOWING
CAT. HYDROCRACKING
MOVING BED CAT. CRACKER
FLUID BED CAT CRACKER
CAT. GASOLINE
FUEL OIL
CATALYTIC REFORMING
ISOMERIZATION
ALKYLATION
POLYMERIZATION
SWEET LIGHT ENDS
WAXES
LUBE STOCKS
SWEET DESULFURIZED RESIDUAL OIL
FINISHED ASPHALT
TO HEAVY HYDROCARBON STORAGE AND BLENDING
COKE
SWEET DESULFURIZED KEROSENE
SWEET KEROSENE
TO MIDDLE DISTILLATE STORAGE AND BLENDING
SWEET DESULFURIZED NAPHTHA
AROMATICS
REFORMATE
ISOMERATE
ALKYLATE
POLY GASOLINE
TO GASOLINE AND PETROCHEMICAL STORAGE AND BLENDING

Figure 5.3-1. Major processing steps in a typical petroleum refinery.[1]

best copy available

Removal of sulfur from some refinery streams is a part of refining. It would be desirable to remove all sulfur compounds before any processing of the crude begins, but because this is impractical, sulfur is removed throughout the refining process. There are several reasons, besides air pollution control, for removing sulfur from intermediate fractions and products of crude oil. Sulfur removal reduces corrosion, odor, occurrence of breakdowns, catalyst poisoning, and gum formation and improves octane rating, color, and lube oil life.[4]

5.3.1 Process Descriptions and Emissions Sources

Most oil refinery processing units are made up of at least five main types of equipment: heaters, reactors, vessels, heat exchangers, and pumps. The arrangement, type, and quantity of equipment are selected to fit the specified function.

5.3.1.1 Refinery Combustion Processes--

In many instances refinery SO_2 emissions come from organic sulfur compounds in the fuel burned as energy sources for process heaters and refinery boilers. Almost every major processing unit in an oil refinery includes one or more process heaters, fired with such fuels as refinery gas, natural gas, and heavy residual fuel oil. Sulfur dioxide concentrations ranging from 700 to 1000 parts per million have been measured in flue gas resulting from burning heavy residual fuel oil.[5] The SO_2 concentrations in the flue gas of boilers and heaters depend entirely on the sulfur content of the fuel.

5.3.1.2 Coking Facilities--

Coking is a severe form of thermal cracking. The feedstock is a residual that may resist cracking by other methods. Coking is an ultimate-yield destructive distillation process, which produces gas, distillate, and coke. Coking is done by two principal processes, the fluid and the delayed.

In fluid coking the feed is sprayed into a reactor containing a fluidized bed of preheated recycled coke particles. The hydrocarbons in the liquid feed crack and vaporize while the nonvolatile material is deposited on the fluidized coke particles. As the size of the coke particles increases, they sink to the bottom of the reactor and flow to a burner. In the burner, the particles are fluidized with air, partially burned, and recycled into the reactor. A portion of the coke produced in the reactor is withdrawn as product. The flue gas from the burner is discharged through the stack after passing through a cyclone.

The vaporized products formed in the reactor are removed from the bed, passing through cyclones that remove some of the coke to the bottom of the scrubber. The heavier gases are condensed, forming a slurry with the coke dust, which is recycled to the reactor. The remaining gases pass to the fractionation zone of the scrubber. The heavy distillate is withdrawn to be fed to the catalytic cracker, and the other gas and distillate products are removed from the system.

The residual feedstock to the coker usually contains the highest weight percent of sulfur of the products leaving the main distillation fractionation column. Thus the various coker products contain sulfur-bearing compounds and must be treated further downstream. The major source of SO_2 emissions in the fluidized coking process is flue gas from the burner. The quantity of emissions depends on the sulfur content of the fuel and the coke.

In delayed coking the coker feed is fed to the bottom section of a fractionator, where the lighter fractions are flashed off. The remaining material is mixed with a recycle stream of heavy products and pumped to the coking heater. The heated feed is passed to the coking drum, where cracking occurs. As the process progresses, the cracked products are removed at the top and coke forms along the inner surface of the drum. The major SO_2 emission point in the delayed coking process is from the heater, depending on the type of fuel used. A liquid waste stream containing hydrogen sulfide (H_2S) is drawn from the overhead accumulator on the coker tower. This stream is pumped to the sour water stripper for H_2S removal. Flaring of gases from blowdown of coke drums will also release SO_2. Some cokers used closed systems or amine scrubbers for SO_2 control.

5.3.1.3 Cracking Processes--

Cracking of large hydrocarbon molecules into smaller ones is accomplished by the application of heat and/or catalysis. At the same time some of the cracked molecules recombine to form larger molecules; the result is formation of a synthetic crude that can be separated into gaseous hydrocarbons, gasoline, gas oil, and fuel. The two kinds of cracking are thermal and catalytic.

Thermal cracking, at high temperature and pressure, is generally applied to distillates heavier than gasoline. In addition to coking operations, visbreaking is an example of a thermal cracking process.

Visbreaking, a milder form of thermal cracking than coking, is used to reduce the viscosity of some residual fractions so that they may be blended into fuel oils. The reduced crude is preheated by heat exchange with visbroken fuel oil and fed to a furnace. Mild cracking in the furnace tubes produces a mixture of residual oil, naphtha, and gas. The reaction products are quenched and fractionated in a steam distillation tower. A sour water waste stream containing H_2S is withdrawn from the fractionator and sent to a sour water stripper for processing.

Catalytic cracking uses high temperatures and chemical catalysts to crack the molecules of gas oils into lighter gasoline material. Two well-known catalytic devices are in use today, the fluid catalytic cracker (FCC) and the thermofor catalytic cracker (TCC). The TCC is no longer generally manufactured. In the FCC, preheated feedstocks are introduced into the bottom of a riser with regenerated catalyst. Most cracking occurs in the riser, and the catalyst is separated from the gaseous reaction products in the reactor vessel. The reaction products flow on to cooling and separation processes. Spent catalyst falls through a steam stripping section (to remove volatile hydrocarbons) and into a regenerator. Controlled combustion of the coke on the catalyst is carried out in the regenerator, and regenerated catalyst is returned to the riser to complete the catalyst cycle. Regenerator flue gas is usually sent to a carbon monoxide (CO) boiler for waste heat recovery before discharge to the atmosphere. The boiler recovers heat from the oxidation of CO to carbon dioxide (CO_2) while reducing emissions of CO. Newer FCC unit designs do not require CO boilers. This flue gas is the major source of SO_2 emission from the catalytic cracker. Sulfur dioxide concentrations in the FCC flue gas range from 150 to 3000 ppm,[6] depending on the amount of sulfur in the feedstock and on operating conditions.

5.3.1.4 Hydrocracking--

Hydrocrackers perform both cracking and hydrogenation and are used to convert heavy feedstocks into lighter, more valuable products. Hydrocracking is done at high pressure and temperature, with a special catalyst and hydrogen. The reaction section is usually divided into two stages. The first stage is designed to remove sulfur and nitrogen compounds by hydrogenating them to hydrogen sulfide and ammonia in a fixed-bed reactor. The second stage accomplishes the actual cracking of the feedstock. The stream from the second stage reactor is fed to a fractionator, where the desired products are separated and recovered. The hydrocracker generates liquid waste streams containing dissolved H_2S from the separators and accumulator. The H_2S in these streams is usually removed in a sour water stripper and further processed in a sulfur recovery unit.

5.3.1.5 Alkylation and Spent Acid Regeneration--

Refinery alkylation is the chemical combination of two light hydrocarbon molecules (an olefin and an isoparaffin) to form one molecule that is in the gasoline boiling range and exhibits good octane characteristics. The feedstocks are catalytically reacted over either anhydrous hydrofluoric acid or sulfuric acid to produce a high-octane component known as alkylate. The reactor effluent is separated into hydrocarbon and acid phases in a settler. The acid is returned to the reactor. From this point on, the alkylate is treated differently in the two processes. In the hydrofluoric acid process, the alkylate and excess isoparaffin are sent to a stripper for separation. An alkylate bottoms stream is charged to a fired heater to decompose any organic fluorides that may have formed. The remaining alkylate from the fired heater is the finished product. In the sulfuric acid process, the hydrocarbon liquid from the settler is washed with caustic and water before being fractionated. The alkylate product is then separated from the isoparaffin, which is returned to the feed stream.

Because the alkylation process is a closed system with no process vents to the atmosphere, SO_2 emissions are negligible. Liquid wastes associated with the water and caustic scrubbing in the sulfuric acid process are generally treated in the refinery wastewater treatment plant. The hydrofluoric acid system produces a sludge waste from the bottoms of the acid regenerator that is readily burned as fuel.

Some refineries regenerate the spent sulfuric acid used in alkylation and treating processes. The spent acid is burned with elemental sulfur and/or hydrogen sulfide gas to form sulfur dioxide. The SO_2 and other combustion products are passed through gas-cleaning and mist-removal equipment, then through a drying tower and on to a sulfur trioxide converter. The SO_3 is absorbed in a circulating stream of concentrated sulfuric acid, which has a concentration of 98 to 99 percent. The nonabsorbed tail gases pass overhead through mist-removal equipment to the exit gas stack. Airborne emissions from spent acid regeneration include SO_2 and acid mist. Acid mist is formed when SO_3 combines with water vapor at a temperature below the dewpoint of H_2SO_4. Sulfur dioxide emissions, an inverse function of the sulfur conversion efficiency, can be as high as 35 kg/Mg (70 lb/ton) of acid produced (95 percent conversion). Acid mist emissions range from 1.1 to 1.4 kg/Mg (2.2 to 2.7 lb/ton) of acid produced.[7] Sulfur dioxide emissions can be controlled by increasing the plant conversion efficiency or by adding a sodium sulfite-bisulfite scrubbing process.[8] Acid mist emissions are reduced by passing the exit gases through an electrostatic precipitator (ESP) or fiber mist eliminators.

5.3.1.6 Oil Desulfurization Processes--

Hydrotreating is used to remove sulfur from all types of petroleum products, eliminate other impurities such as nitrogen and oxygen, decolorize and stabilize products, and correct odor problems and many other product deficiencies. This widely used process consists of bringing oil charge stock and hydrogen into a fixed-bed, catalytic reactor at high temperature and pressure. Hydrogen reacts with sulfur, nitrogen, oxygen, and olefinic hydrocarbons to form removable hydrogen sulfide, ammonia, saturated hydrocarbons, and water. The process gas is rich in hydrogen, hydrocarbons, and hydrogen sulfide. The H_2S can be extracted from the stream and converted to elemental sulfur or sulfuric acid. The catalyst in a hydrodesulfurization process is regenerated periodically to remove built-up coke. During regeneration, a steam-air mixture burns off the undesirable carbon buildup; sulfur dioxide is released to the atmosphere during this process or is contained in a closed cycle regeneration system.

5.3.1.7 Sulfur Recovery Units--

Refinery sour gas streams are generally fed to a regenerative type of hydrogen sulfide removal process. The concentrated acid gas is then sent to the sulfur recovery unit (SRU). The Claus process (developed in about 1890) is the most widely used method of producing sulfur from refinery hydrogen sulfide. The modified Claus process (developed in about 1937) is based on producing elemental sulfur by first converting one-third of the hydrogen sulfide feed by precise combustion with air to achieve the following reaction:

$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O.$$

The above products of combustion are then allowed to react thermally with the remaining two-thirds of the hydrogen sulfide feed in the presence of a suitable catalyst to form sulfur vapor:

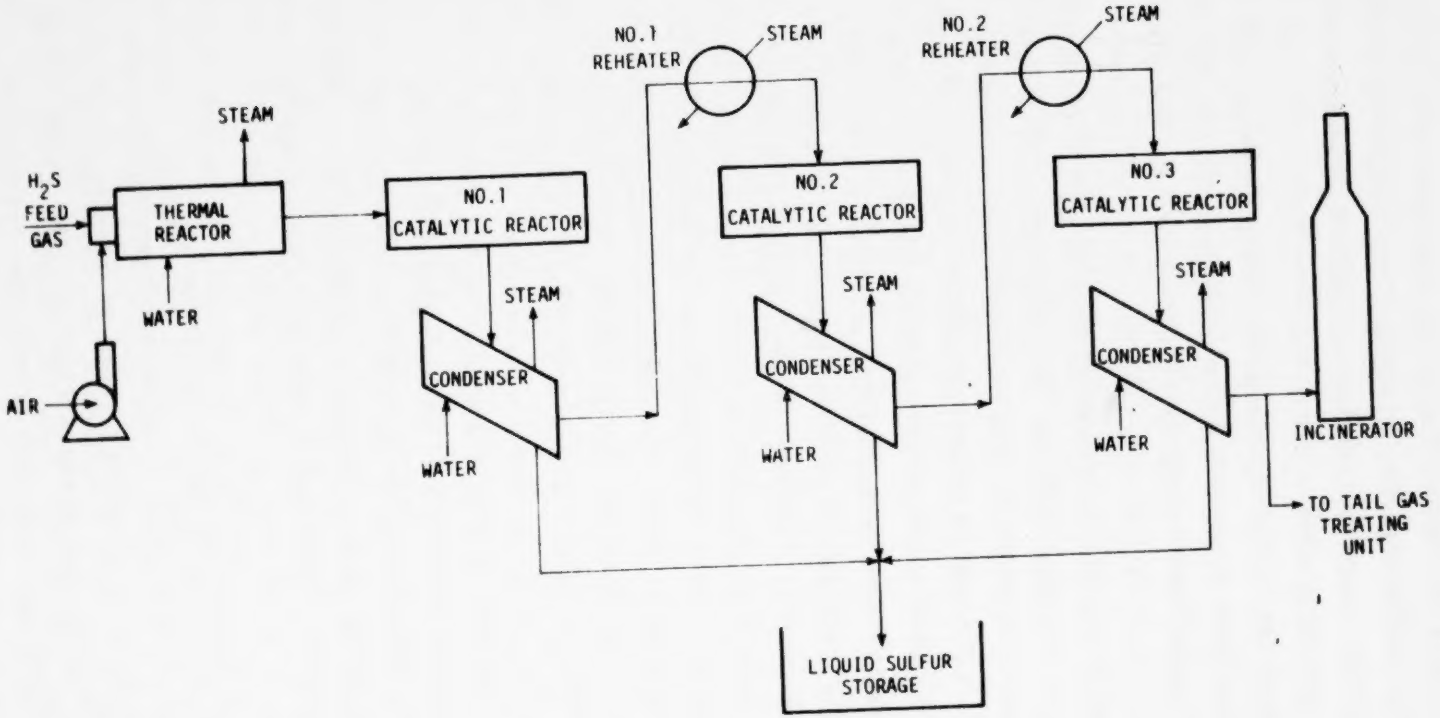
$$2H_2S + SO_2 \rightarrow aS_2 + bS_6 + cS_8 + 2H_2O.$$

The letters "a," "b," and "c" represent the number of moles of the various possible molecular forms of sulfur vapor. The sulfur is recovered by cooling the gas to condense the sulfur. In addition to these reactions, some sulfur is produced directly by dissociation of hydrogen sulfide:

$$H_2S \rightarrow H_2 + 1/2S_2.$$

This is a minor reaction, however, and does not contribute appreciably to the overall sulfur recovery.

Figure 5.3-2 shows a typical Claus process employing both noncatalytic (thermal) and catalytic reaction. Generally about 50 to 60 percent of the feed sulfur is recovered in the sulfur condenser following the noncatalytic or thermal reaction. Following the oxidation (combustion) reaction in the thermal reactor, the hot gases are fed to a waste heat boiler, where steam is generated. The cooled gases from the waste heat boiler are fed to the first sulfur condenser, where the elemental sulfur made in the thermal reactor is condensed. The uncondensed gases leave the first sulfur condenser and are heated prior to being fed to the first catalytic reactor. The gases must be heated above the sulfur dewpoint to prevent sulfur condensation on the catalyst and to obtain the optimum sulfur recovery in the


NO.1
REHEATER
STEAM
NO.2
REHEATER
STEAM
STEAM
H_2S
FEED
GAS
THERMAL
REACTOR
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NO.1
CATALYTIC REACTOR
STEAM
CONDENSER
WATER
NO.2
CATALYTIC REACTOR
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CONDENSER
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NO.3
CATALYTIC REACTOR
STEAM
CONDENSER
WATER
INCINERATOR
TO TAIL GAS
TREATING
UNIT
LIQUID SULFUR
STORAGE

Figure 5.3-2. Sulfur recovery unit.

reactor. A fixed-bed catalytic reactor containing activated alumina (Al_2O_3) catalyst is used to improve the sulfur recovery. The sulfur-laden gases are then fed to another sulfur condenser for recovery of the molten sulfur. This reheating, reaction, condensing cycle is repeated with each catalytic reactor on the Claus unit.

Following the sulfur condensation step, the remaining gases are fed to an incinerator, in which all sulfur compounds in the tail gas are converted to SO_2 by combustion before being discharged to the atmosphere through a stack.

The overall sulfur recovery obtainable with a Claus plant is dependent on the number of catalytic reactors, hydrogen sulfide concentration in the feed, degree of carbon dioxide and hydrocarbon contamination in the feed gas, and outlet temperature of the sulfur condensers. In the past, sulfur recovery units were operated with only one catalytic reactor. This practice is not commonly used today because with only one catalytic reactor the overall sulfur recovery is limited to about 75 percent. A minimum of two catalytic reactors is required to provide overall sulfur recovery of about 90 percent, and the maximum level of overall sulfur recovery with three catalytic reactors is considered to be 97 percent.[9] Although some Claus units have been built with four catalytic reactors, this generally is not done because of the reaction limitations.[10]

The Claus unit tail gas contains sulfur dioxide, hydrogen sulfide, elemental sulfur, carbonyl sulfide, and carbon disulfide. Incineration of the tail gas converts all of the sulfur to SO_2 before it is emitted to the atmosphere through the stack. The concentration of SO_2 in the stack gases depends on the overall sulfur recovery in the Claus unit, the incineration temperature, and the amount of excess combustion air. The SO_2 concentration can range between 3,000 and 20,000 ppm, but normally averages 8000 to 12,000 ppm.[9]

5.3.1.8 Other Sulfur Oxide Emission Sources--

Separation of a mixture of light and heavy hydrocarbons into fractions or intermediates of a specified range of boiling temperatures is usually done by distillation and steam stripping. The crude charge is separated into several petroleum fractions within the fractionator. Several liquid side streams are withdrawn from the fractionator at different elevations within the tower. The fractions are charged to the side-stream product stripper, where lighter hydrocarbons are stripped and returned to the fractionation tower. The stripping medium is usually steam or light petroleum gas. In addition to the side-stream strippers, the crude distillation column has a bottoms stripping zone, in which lighter hydrocarbons are steam-stripped from the residual product. Almost every major processing unit in the refinery includes a distillation section. Atmospheric distillation is a closed process with only fugitive air emissions. Sour water containing sulfides is produced from the condensed stripping steam and is sent to the sour water stripper for removal of hydrogen sulfide.

Catalytic reforming units are used to convert low-octane naphthas into high-octane blending stocks to be used in production of gasoline. Reforming is accomplished by rearranging the molecular structure of the feedstock. Reformer feedstock in the presence of hydrogen reacts over a platinum-rhenium catalyst. Hydrogen is produced and partly recycled to the reactor; the excess is used in hydrogen treating units for sulfur removal and product improvement. This process unit is a closed system. Although SO_2 emissions can occur during catalyst regeneration, this happens rarely, and the emissions are considered negligible. Some catalytic reforming units incorporate a continuous catalyst regeneration system. Total emissions, including SO_2, average from 0.006 to 0.06 g/liter (0.002 to 0.02 lb/bbl)[11] and are considered negligible.

Waste gas from a refinery is generally odorous and can be handled by one or more flare systems. The sulfur content of the waste gas to each flare system depends on its source, because it can come from one or more refinery operating units. The combustible composition of waste gas and the temperature in the combustion zone determine the effectiveness of the control system. Sulfur dioxide and other injurious substances in hydrocarbon waste gases should be removed by some type of absorption system before going to a flare. Absorption systems for relief valves, however, may not be practical because of the erratic nature and rates of release.

Vacuum distillation separates the atmospheric residue from the main fractionator into a heavy residual oil and one or more heavy gas oil streams. Vacuum fractionators are maintained at approximately 100 mm mercury (Hg) absolute pressure by either steam ejectors or mechanical vacuum pumps. Noncondensable vapors removed by these systems must be discharged. The vapor emissions, containing as much as 25 percent hydrogen sulfide by volume, may be as high as 400 g/1000 liters (130 lb/1000 bbl) of vacuum unit charge. In addition, aqueous wastes containing hydrogen sulfide result from condensation of steam used for stripping during vacuum fractionation and for maintaining fractionator vacuum by ejectors.

Asphalt from the crude refining unit can be made into roofing asphalt by subjecting it to air blowing at elevated temperatures. Air is passed through the charge in a steam-blanketed still at an approximate rate of 1.2 m^3/min per Mg (40 ft^3/min per ton) of charge until the desired hardness is achieved. The overhead gas, rich in hydrocarbon vapors, is sent to a knockout drum. Gas from the knockout drum flows to an incinerator. The effluent stream contains negligible amounts of various sulfur compounds.

Treating is used in refinery processing to remove undesirable impurities such as sulfur, nitrogen, and oxygen to improve product quality. Emissions from treating operations consist of sulfur dioxide, hydrocarbons, and visible plumes. Emission levels depend on the methods used in handling spent acid and acid sludges, as well as in recovering or disposing of hydrogen sulfide. As refineries continue to process increasing amounts of high-sulfur crudes, chemical treating of final products is being replaced by hydrogen desulfurization of many feedstocks.

5.3.2 Control Techniques

5.3.2.1 Description--

Four processing areas within a refinery generate the major sulfur emissions:

1) Process heaters and boilers

2) The fluid catalytic cracking unit

3) The sulfur recovery unit

4) Flares burning H_2S streams.

Process heaters and refinery boilers are integral parts of almost every processing unit in a refinery. Fuel requirements for heaters and boilers range between 5 and 10 percent of the heating value of the crude that enters the refinery.[12] Sulfur dioxide emissions depend on the sulfur content of the fuel. Concentrations of SO_2 emitted from heaters and boilers can be reduced by burning low-sulfur fuel oil, low-sulfur process gas, or natural gas. Flue gas desulfurization techniques are not currently applied to process heaters or boilers, but are described in Section 4.2.

The removal of SO_2 from the regeneration gases of FCC and TCC units is not widely practiced. Studies in the literature for reduction of SO_2 emissions from FCC regeneration flue gas suggest several alternatives:[13]

1) Desulfurization of FCC feed.

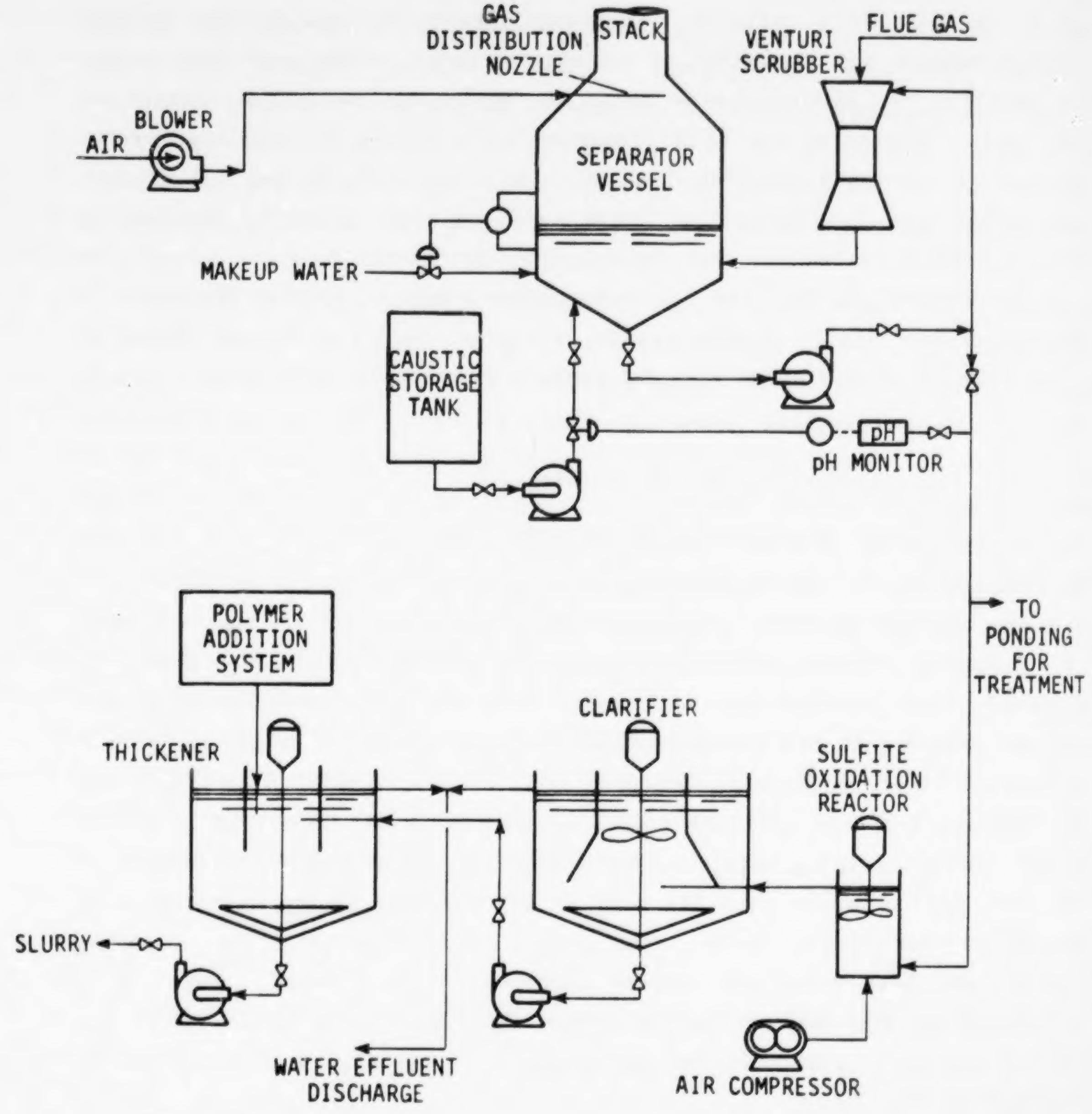
2) Flue gas desulfurization techniques.

3) Specific catalysts for SO_2 emission control.[14]

Desulfurization of FCC feed is practiced on a limited basis and usually is done to improve gasoline yield and reduce coke buildup on the catalyst.

A flue gas desulfurization system, developed and marketed by Exxon, is currently used in four Exxon FCC units. This is an application of a jet-ejector liquid scrubber for simultaneous removal of sulfur oxides and particulates.[15] The schematic for Exxon's jet ejector scrubbing system is shown in Figure 5.3-3. An alkaline scrubbing medium, usually a sodium solution, passes through a spray nozzle, which breaks the liquid stream into droplets. The flue gas is drawn into the body of the scrubber by the draft-inducing action of the liquid spray. The gas is intermixed with the scrubbing liquid, and both enter the venturi section of the scrubber. The intense turbulence in the venturi section causes the liquid droplets to strike and capture the particulates in the gas stream, and the SO_2 in the flue gas is absorbed in the liquid.

The mixture of gas and liquid droplets is sent to a separator, where the clean gas is separated from the contacted liquid and discharged to the atmosphere. The purge stream from the scrubber will contain suspended solids (catalyst) and soluble sulfite and sulfate salts. It is necessary to treat the scrubber bleed before it can be discharged. The water treatment should include removal of insoluble salts, reduction of chemical oxygen demand, and reduction of soluble salts.


GAS
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VENTURI
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AIR
BLOWER
SEPARATOR
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CLARIFIER
THICKENER
SULFITE
OXIDATION
REACTOR
SLURRY
WATER EFFLUENT
DISCHARGE
AIR COMPRESSOR

Figure 5.3-3. Process layout of the venturi scrubbing system.

At locations where the FCC regenerator is operated at hot regeneration or where sufficient pressure is available, the jet-ejector venturis can be replaced by high-energy venturi scrubbers.

Pilot plant performance data show efficiencies of 95 to 99 percent for removal of sulfur oxides from an inlet gas stream with 200 to 500 ppm SO_2 and 85 to 95 percent for removal of particulates.[15] Recent sulfur dioxide sampling tests conducted by the Texas Air Control Board (TACB) on the [illegible] FCC units at the Exxon Baytown Refinery indicate a scrubber efficiency of 94 percent for SO_2 removal from an inlet gas stream with 900 to 1040 ppm SO_2.[16]

Special cracking catalyst composition can also reduce regenerator flue gas sulfur oxide emissions by adsorbing SO_2 onto the catalyst surface. Basically, SO_2 is oxidized to SO_3 in the regenerator, absorbed on the catalyst surface as the sulfate (SO_4), and then carried into the reactor where it is reduced in the cracking reaction to H_2S; the H_2S then exits the system with the cracked products. Special catalysts used to achieve SO_x reduction in both pilot unit and commercial trials have shown flue gas SO_2 reductions of up to 88 percent.[17]

Tail gas from the sulfur recovery unit is a major sulfur source in a refinery and usually requires SO_2 control. Emissions can be as high as 20,000 ppm, but normally average 10,000 ppm. Air quality control restrictions normally require the use of a Claus plant tail-gas treating unit for further reduction of SO_2 emissions. Operational tail-gas control systems include the IFP-1500 process, the Sulfreen process, the Beavon process, the Stretford process, the Shell Claus off-gas treating (SCOT) system, and the Wellman-Lord process.

IFP-1500 process--The IFP-1500 process converts mixed hydrogen sulfide/sulfur dioxide streams to sulfur and water by a liquid-phase Claus reaction using a proprietary catalyst. The process is primarily used to clean Claus unit tail gas. The technology is an extension of the Claus reduction process, but is carried out in the liquid phase. In this process the tail gas, at Claus unit exit pressure, is injected into the bottom of a packed tower, where the packing provides necessary surface area for gas-liquid contact. A low-vapor-pressure polyethylene glycol solvent containing a proprietary carboxylic acid salt catalyst in solution circulates countercurrently to the gas.

The catalyst forms a complex with H_2S and SO_2, which in turn reacts with more of the gases to regenerate the catalyst and form elemental sulfur. The reaction is exothermic, and the heat released is removed by injecting and vaporizing steam condensate. Temperature is maintained at about 120° to 132°C (250° to 270°F), high enough to keep the sulfur molten but not high enough to cause much loss of sulfur or glycol overhead. The sulfur accumulates in the boot of the tower and is drawn off continuously through a seal leg. Overhead gases from the IFP-1500 unit are incinerated.

The vendor claims that the IFP-1500 process is insensitive to changes in gas flow rates. It has been shown to operate at flows as low as 30 percent of design without adverse effect. Another stated advantage is maintenance-free operation for about 24 continuous months, after which the unit is shut down to wash away spent catalyst that deposits on the packing material. A water wash is all that is required. Outlet SO_2 concentration is 1000 to 2000 ppm.[18]

Sulfreen process--The Sulfreen process reduces the sulfur content in Claus plant tail gas by further promoting the Claus reaction on a catalytic surface in a gas/solid batch reactor. Claus tail gas is first scrubbed with liquid to wash out entrained sulfur liquid and sulfur vapor. The tail gas is then introduced to a battery of reactors, where the Claus reactions are carried out at lower temperatures (127° to 149°C, 260° to 300°F) than those utilized in the sulfur plant.

A regeneration gas, essentially nitrogen, periodically desorbs the sulfur-laden catalyst beds. Nitrogen is heated and cycles through the catalyst bed at approximately 300°C (570°F) until all water and CO_2 are driven off.

The process reduces entrained sulfur, because the catalyst acts as an absorbent for liquid sulfur. Tail gas passing through the catalyst bed, however, retains several hundred parts per million of sulfur vapor in equilibrium with liquid sulfur. The H_2S and SO_2 are reduced by 80 to 85 percent to levels of about 1800 ppm H_2S and 900 ppm SO_2. As with the IFP-1500 process, the levels of H_2S and SO_2 are highly dependent upon maintaining the 2:1 ratio of H_2S to SO_2 in the Claus tail gas. Carbonyl sulfide and carbon sulfide are not affected by the Sulfreen process.

Beavon process--The Beavon process is a reduction-type tail-gas treatment system. As a first step, all sulfur compounds in the Claus tail gas are converted to hydrogen sulfide. This process takes place in a fixed-bed reactor, in which a cobalt-molybdenum catalyst enhances the reaction. Before the reactor, however, a fuel gas stream is combusted in an in-line burner and mixed with the Claus tail gases to provide a reducing atmosphere. Hydrogenation and hydrolysis reactions reduce all sulfur (as carbonyl sulfide, carbon disulfide, sulfur, and SO_2) to hydrogen sulfide.

The following reactions are involved in this step:

$$S_8 + 8H_2 \rightarrow 8H_2S$$
$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$
$$COS + H_2O \rightarrow H_2S + CO_2$$
$$CS_2 + H_2O \rightarrow H_2S + COS$$
$$CS_2 + 2H_2S \rightarrow CH_4 + 4S$$
$$4H_2 + CS_2 \rightarrow 2H_2S + CH_4$$
$$COS + 4H_2 \rightarrow H_2O + H_2S + CH_4.$$

The stream from this reaction step, rich in hydrogen sulfide, is dewatered by direct contact cooling in a quench tower. The sour water must be cleaned in a sour water stripper facility. The hydrogenated tail gas is fed to a Stretford unit for sulfur recovery.

Stretford process--Although the Stretford process may be capable of solely replacing Claus or amine sulfur removal processes, it has gained more recognition as part of the Beavon tail-gas cleanup process.

Sour fuel gas or Claus tail gas is fed to the hydrogen sulfide absorber column that contains "Stretford solution." This is a solution of sodium vanadate ($NaVO_3$) and sodium carbonate (Na_2CO_3). The hydrogen sulfide is absorbed by the sodium carbonate in the reaction:

$$H_2S + Na_2CO_3 \rightarrow NaHS + NaHCO_3.$$

It is precipitated by reaction with the $NaVO_3$:

$$2NaVO_3 + NaHS + NaHCO_3 \rightarrow S + Na_2V_2O_5 + Na_2CO_3 + H_22O.$$

The sodium vanadate is regenerated by use of an acid called ADA (antraquinone disulfonic acid) by the reaction:

$$Na_2V_2O_5 + \text{ADA (oxidized)} \rightarrow 2NaVO_3 + \text{ADA (reduced)}.$$

The ADA is regenerated to an oxidized state by bubbling air through the solution. After the absorption step, the Stretford solution is held in a tank for a period of time to promote sulfur precipitation. As a result of the air bubbling step, the sulfur is floated to the surface of the solution, and the froth overflows into a settling tank. Sulfur is recovered from this tank as a sludge, which is filtered to form sulfur cakes; the cakes are dewatered in an autoclave separator. The resultant liquid sulfur is removed for storage and/or sale. Overall sulfur recovery of the Claus process plus the Beavon-Stretford process is over 99.9 percent. Typical sulfur emissions are less than 50 ppm.[19]

SCOT process--The SCOT system is a reduction-type SO_2 control system. The first commercial-scale SCOT units in the United States began operations in early 1973.

In the initial phase of treatment the Claus tail gas is subjected to reactions that convert all of the sulfur-containing compounds to hydrogen sulfide. This initial phase is identical to that of the Beavon process for controlling Claus emissions. An in-line burner heats the tail gas, and a reducing atmosphere is maintained. A cobalt-molybdenum (on alumina) catalyst in the fixed-bed reactor enhances conversion of the materials to hydrogen sulfide by the following reactions:

$$S + H_2 \rightarrow H_2S$$

$$SO_2 + 3H_2 \rightarrow H_2S + 2H_2O$$

$$COS + H_2O \rightarrow H_2S + CO_2$$

$$CS_2 + 2H_2O \rightarrow 2H_2S + CO_2.$$

The gas is cooled to near ambient temperature by direct contact with water (or air) in a packed quenching tower. Sour water condenses from the stream of H_2S-rich gas and is withdrawn. The sulfur in this sour water must be removed before the water can be disposed of. An onsite sour water stripper may be used for this purpose; or a stripper may be installed as an integral part of the SCOT system.

The cooled gas stream is piped to a tray tower absorber, where diisopropanolamine absorbs the hydrogen sulfide and carbon dioxide from the stream. The amine, laden with hydrogen sulfide, is sent to a regenerator, which is normally a conventional steam stripping column. The regenerator off-gas (hydrogen sulfide and carbon dioxide) is recycled to the Claus plant as feed material. Absorber off-gas containing less than 300 ppm hydrogen sulfide is incinerated before release through the stack.

Wellman-Lord process--In the Wellman-Lord process, the SO_2-rich gas is stripped of SO_2 in a countercurrent absorber containing a sodium sulfite solution. The spent solution, rich in bisulfite, is discharged to a surge tank and then pumped to a proprietary evaporator/crystallizer in the regeneration section. Low-pressure steam is used to heat the evaporator and to drive off SO_2 and water vapor. The sodium sulfite precipitates as a dense slurry of crystals.

The gas stream leaving the evaporator is subjected to partial condensation to remove most of the water vapor before the product SO_2 is discharged from the process. The final product SO_2 can be delivered at whatever quality is required for further processing. It is suitable for conversion to high-grade sulfuric acid or elemental sulfur.

The condensate is mixed with the sulfite slurry stream withdrawn from the evaporator and is used for redissolving the slurry. The sulfite-lean solution is them pumped to a surge tank and fed back to the absorber.

The process is based on a sodium sulfite/bisulfite cycle. The reactions in the process can be abbreviated for simplicity as follows:

$$\text{Absorption} \quad SO_2 + Na_2SO_3 + H_2O \rightarrow 2NaHSO_3$$

$$\text{Regeneration} \quad 2NaHSO_3 \rightarrow Na_2SO_3\downarrow + SO_2\uparrow + H_2O\uparrow.$$

Apart from the two major reactions above, sodium sulfate (Na_2SO_4), which is nonregenerable, is formed in the absorber as a result of solution contact with oxygen and sulfur trioxide. The sodium sulfate so formed is controlled by maintaining a continuous purge from the system. A makeup of caustic is required to replace that lost in the purge stream. The absorber off-gas normally contains less than 250 ppm SO_2 and is vented to the atmosphere.[20]

5.3.2.2 Control Cost--

Marketing brochures published by Exxon have compared the cost of a flue gas scrubbing unit with the cost of a feed hydrodesulfurization (HDS) unit/ electrostatic precipitator for a fluid catalytic cracking unit with a capacity of 13.3 x 10^6 liters (80,000 bbl) per day at a Gulf Coast refinery.[21] Independent estimates adjusted to mid-1979 dollars indicate that the base case of a feed HDS unit/ESP would require $7,000,000 for capital investment and $800,000 for annual operating expenses.[22-25] Exxon estimated that the capital investment for the jet ejector flue gas scrubbing system, including a heating oil HDS unit, was two-thirds the capital investment required for the base case of a feed HDS unit/ESP and that the annual operating cost of the flue gas scrubbing system was one-half the annual operating expense of the base case. The investment and operating costs would be lower if a high-energy venturi were used in place of the jet ejector venturi. The operating costs did not include increased gasoline yield credits resulting from the improvement of feed quality gained through HDS. Actual capital and operating costs of the Exxon units are considered proprietary information and were not divulged.

Because of legislation requiring the reduction of SO_2 emissions from sulfur recovery units, most refineries must provide tail-gas treating units. The cost of recovering this incremental sulfur is high and varies from 50 to over 100 percent of the cost of a new Claus unit.[26] Tables 5.3-1 to 5.3-3 show the typical capital and operating costs of tail-gas treating units. These estimates are not firm because costs vary with location, process differences that affect energy requirements, need for chemicals and supplies, and regenerability of the catalyst.

5.3.2.3 Energy and Environmental Impact[27]--

Refinery sulfur plants are major point sources of sulfur dioxide emissions within petroleum refineries. These emissions result from treatment of the gases produced by various sulfur removal processes within the refinery. A typical uncontrolled sulfur plant (two- or three-stage Claus plant) recovers about 95 percent of the sulfur in the incoming gas stream. Thus, emissions of sulfur dioxide are usually in the range of 8,000 to 10,000 ppm.

TABLE 5.3-1. ANNUAL COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH INCINERATION[28]
(June 1979 dollars)

	Plant size, Mg/day (long tons/day)		
	5 (5)	10 (10)	102 (100)
Manpower per shift	½	½	½
Direct labor (DL) at $7.70/h	$ 33,800	$ 33,800	$ 33,800
Supv. and fringes at 40% DL	13,500	13,500	13,500
Electric power at $0.05/kWh[a]	3,000	5,800	58,800
Fuel at $2.00/1000 ft^3 of natural gas	7,000	13,700	137,700
Maintenance at 3% of investment	29,500	35,190	108,500
Steam credit at $3.00/1000 lb	(32,400)	(64,800)	(650,400)
Sulfur credit at $50/long ton[b]	(83,000)	(166,000)	(1,660,000)
Net operating cost	(28,600)	(128,810)	(1,958,100)
Capital charges at 17% of investment[c]	167,300	199,400	615,100
Total annual cost	$138,700	$ 70,590	$1,343,000
Investment	$984,000	$1,173,000	$3,618,000

[a] 350 operating days per year.

[b] Assumes 95% recovery.

[c] Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance, and G&A.

Note: Long ton = 2240 pounds.

TABLE 5.3-2. COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH WELLMAN-LORD EMISSION CONTROL SYSTEM (OXIDATION)[29]
(June 1979 dollars)

	Plant size, Mg/day (long tons/day)		
	5 (5)	10 (10)	102 (100)
Manpower per shift	2	2	2
Direct labor at $7.70/h	$ 135,000	$ 135,000	$ 135,000
Supv. and fringes at 40% DL	54,000	54,000	54,000
Electric power at $0.05/kWh[a]	6,300	12,700	126,000
Fuel at $2.00/1000 ft^3	7,000	13,700	137,700
Maintenance at 3% Inv. (Claus)	28,500	34,000	106,600
at 5% Inv. (Wellman-Lord)	23,800	29,200	177,700
Chemicals at $260/ton 50% NaOH	4,600	9,100	91,000
Soft water at $0.80/1000 gal	300	500	4,500
Steam credit at $3.00/1000 lb	(28,800)	(57,600)	(257,100)
Sulfur credit at $50/long ton[b]	(87,400)	(175,000)	(1,750,000)
Net operating cost	143,300	55,600	(1,174,600)
Capital charges at 17% Inv.[c]	242,100	291,800	999,100
Total annual cost	385,400	347,400	(175,500)
Investment (Claus less Incin.)[d]	949,000	1,132,000	3,553,000
	475,000	584,000	2,324,000
Total investment[e]	$1,424,000	$1,716,000	$5,877,000

[a] 350 operating days per year.

[b] Assumes 100% sulfur recovery with tail gas unit.

[c] Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance, and G&A.

[d] Incinerator adjustment from, "Air Pollution Control Technology and Costs in Seven Selected Areas," Report No. EPA-450/3-73-010, page 629.

[e] 6/79 Chem. Eng. Index.

TABLE 5.3-3. COSTS FOR CLAUS SULFUR RECOVERY PLANTS WITH BEAVON EMISSION CONTROL SYSTEM (REDUCTION)[30]
(June 1979 dollars)

	Plant size, Mg/day (long tons/day)		
	5 (5)	10 (10)	102 (100)
Manpower per shift	2	2	2
Direct labor at $7.70/h	$ 135,000	$ 135,000	$ 135,000
Supv. and fringes at 40% DL	54,000	54,000	54,000
Electric power at $0.05/kWh[a]	7,800	15,500	155,300
Fuel at $2.00/1000 ft^3	1,300	3,000	28,700
Maintenance at 3% Inv. (Claus)	28,500	34,000	106,600
at 5% Inv. (Beavon)	47,200	58,100	183,800
Catalyst and chemicals	1,000	2,100	21,400
Soft water at $0.80/1000 gal		300	1,600
Steam credit at $3.00/1000 lb	(32,400)	(64,200)	(642,600)
Sulfur credit at $50/long ton[b]	(87,400)	(175,000)	(1,750,000)
Net operating cost	155,000	62,800	(1,706,200)
Capital charges at 17% Inv.[c]	321,800	390,000	1,228,900
Total annual cost	476,800	452,800	(477,300)
Investment (Claus less Incin.)[d]	949,000	1,132,000	3,553,000
	944,000	1,162,000	3,676,000
Total investment[e]	$1,893,000	$2,294,000	$7,229,000

[a] 350 operating days per year.

[b] Assumes 100% sulfur recovery.

[c] Capital recovery factor for 15 years at 10% interest plus 4% of investment for property taxes, insurance, and G&A.

[d] Incinerator adjustment from, "Air Pollution Control Technology and Costs in Seven Selected Areas," Report No. EPA-450/3-73-010, page 629.

[e] 6/79 Chem. Eng. Index.

The tail-gas scrubbing systems used to reduce emissions from the Claus plant employ oxidation or reduction processes and result in residual emissions of SO_2 (oxidation) or H_2S (reduction). The reduction system generally, however, leads to the overall lowest level of emissions.

Energy impact--Although not generally recognized, petroleum refineries consume a significant amount of energy in processing crude oil into various petroleum products such as petrochemical feedstocks, gasolines, fuel oils, etc. The energy requirements of a typical moderate- or high-conversion refinery, for example, usually represent about 10 percent of the crude oil throughout. Thus, the energy consumption of a nominal 15,900-m^3/day (100,000-bbl/day) refinery is equivalent to about 1590 m^3/day (10,000-bbl/day) of fuel oil, or some 250,000 kWh/h.

The energy requirements of refinery sulfur plants are quite small in comparison. A 102-Mg/day (100-long-ton/day) Claus sulfur plant, for example, typically consumes less than 1000 kWh/h of energy, or less than 0.5 percent of the energy consumed within the petroleum refinery itself. Consequently, the use of Claus sulfur plants to control emissions of sulfur dioxide or hydrogen sulfide at petroleum refineries does not significantly increase the energy requirements associated with petroleum refining.

The energy impact associated with each of the alternative emission control systems is summarized in Table 5.3-4. Tail-gas treating units have a slight energy penalty or a moderate energy benefit, depending on whether an oxidation or reduction tail-gas scrubbing emission control system is employed and on whether tail-gas reheat is required to increase plume bouyancy. The moderate energy benefit associated with the reduction tail gas scrubbing system arises because of reduced tail-gas incineration requirements.

This energy impact will vary from refinery to refinery, depending on whether an oxidation or a reduction tail-gas scrubbing system is employed. As shown in Table 5.3-5, use of an oxidation tail-gas scrubbing system without tail-gas reheat increases the overall energy consumption of a Claus sulfur plant by about 17 percent. Use of a reduction tail-gas scrubbing system without tail-gas reheat, however, reduces the overall energy consumption by about 50 percent.

TABLE 5.3-4. ENERGY IMPACT OF EMISSION CONTROL SYSTEMS[31]

Energy impact[a]	Base case[b]	Tail-gas scrubbing by oxidation system[c]		Tail-gas scrubbing by reduction system[c]	
		Without reheat	With reheat	Without reheat	With reheat
Energy consumption					
Fuel, MW thermal (10 Btu/h)					
Process	2.4 (8.2)	2.4 (8.2)	2.4 (8.2)	0.5 (1.7)[d]	0.5 (1.7)[d]
Incineration			1.7 (5.7)[e]		1.7 (5.7)[e]
Electricity, kWh/h	140	300	300	370	370
Energy credit,[f] kg/s (10^3 lb/h)					
High-pressure steam[g]	2.3 (18)	2.3 (18)	2.3 (18)	2.3 (18)	2.3 (18)
Low-pressure steam[h]	1.0 (7.8)	0.6 (5)	0.6 (5)	0.9 (7.5)	0.9 (7.5)
Total energy consumption without steam credit, kWh/h	960	1120	1690	540	1110
Total energy credit with steam credit, kWh/h	894	950	380	1300	735

[a] Conversions.

Fuel, 0.293 MW thermal (10^6 Btu/h) = 100 kWh/h.
High-pressure steam, 0.126 kg/s (10^3 lb/h) = 90 kWh/h.
Low-pressure steam, 0.126 kg/s (10^3 lb/h) = 30 kWh/h.

[b] 102-Mg/day (100-long-ton/day) Claus sulfur plant.

[c] Includes energy consumption by Claus sulfur plant.

[d] Fuel used to produce reduction gases.

[e] Incineration of sulfur plant tail gases.

[f] Does not include steam that could be produced if tail-gas incinerators were equipped to recover waste heat.

[g] Produced at 3.8 MPa and 400°C (550 psig and 750°F).

[h] Produced at 0.34 MPa (50 psig) and saturated.

Tail-gas treating units will reduce national energy consumption by some 54 million kWh/yr, or about 14,300 m^3 (90,000 bbl) of fuel oil per year, assuming that refinery sulfur plants accounting for half of the capacity subject to compliance with New Source Performance Standards (NSPS) install oxidation tail gas scrubbing systems without tail-gas reheat and that plants accounting for the other half install reduction tail-gas scrubbing systems without tail-gas reheat.

Ambient air quality impact--Tail-gas scrubbing systems reduce the maximum ambient air concentrations of SO_2 to essentially zero for all practical purposes, assuming an oxidation tail-gas scrubbing system is employed. If a reduction tail-gas scrubbing system is employed, emissions of SO_2 are eliminated. Use of a reduction system, however, leads to emissions of H_2S, carbonyl sulfide, and carbon disulfide and thus low ambient air concentrations of these pollutants. Table 5.3-5 shows the calculated sulfur emissions in SO_2 equivalent from a sulfur recovery unit and a reduction tail-gas treating unit.

TABLE 5.3-5. CALCULATED SO_2 EMISSIONS FROM CLAUS AND SCOT UNITS

Sulfur recovery unit capacity, Mg/day (tons/day)	9 (10)	45 (50)
Claus unit emissions (no tail-gas treating unit and 95% sulfur recovery efficiency), g/s (lb/h)	12.5 (98.9)	61.9 (490.9)
SCOT unit emissions (sulfur recovery efficiency increased to 99.5%), g/s (lb/h)	1.2 (9.3)	6.1 (48.5)

Water pollution impact--Petroleum refinery Claus sulfur plants generate a small wastewater stream. This stream results from condensation of water vapor contained in the H_2S gases as they flow from the amine scrubbing units to the Claus sulfur plant. The volume of water involved is less than 0.25 liter (0.07 gal) per minute and normally contains 1500 to 2000 ppm H_2S and up to 1000 ppm ammonia. The refinery's wastewater treatment facilities can easily handle this stream.

The potential water pollution impact of the tail-gas treating units is negligible. Table 5.3-6 summarizes the characteristics and flow rates of the various wastewater streams discharged by these systems. As this table shows, although the volume of wastewater discharged by some of these emission control processes is larger than that discharged by the sulfur recovery unit, it is less than 50 liters (13 gal) per minute.

Generally, the wastewater streams generated by the various tail-gas scrubbing processes consist of a sour water condensate and a purge stream containing either organic or inorganic salts. The amount and composition of these wastewater streams varies depending on the particular tail-gas scrubbing process used. The sour water condensate is produced by cooling of the gases prior to the scrubbing tower, and the purge stream is necessary in most cases to prevent a buildup of impurities in the scrubbing solutions. All the wastewater streams generated by the emission control systems can be treated without difficulty in the refinery's wastewater treatment facility. Because these waste streams are so small, they will have a minor impact on the ability of petroleum refineries to meet water quality effluent regulations.

Solid waste impact--There is essentially no potential solid waste impact associated with tail-gas treating units.

The Claus process itself requires periodic replacement of the reaction catalysts; the frequency of replacement depends upon the impurities present in the acid gas feed. Usually the catalyst, made of bauxite or alumina, is regenerated annually until a substantial loss of activity occurs, normally in 2 to 5 years. Emission control systems will not affect the rate or quantity of catalyst replacement in the Claus plant.

As for the emission control systems themselves, the oxidation tail-gas scrubbing systems do not generate any solid waste. The reduction tail-gas scrubbing systems, however, do require periodic replacement of the reduction catalysts about every 2 years. These catalysts usually have significant salvage value; because they are composed primarily of colbalt-molybdenum, they are normally returned to a vendor for reprocessing. Hence, even the reduction tail-gas scrubbing systems generate essentially no solid waste.

Other environmental impacts--No environmental impacts other than those discussed above are likely to arise from tail-gas treating units for

TABLE 5.3-6. POTENTIAL WATER POLLUTION IMPACT OF REFINERY SULFUR PLANT WITH VARIOUS TAIL-GAS TREATING UNITS[32]

	Waste water source	Amount discharged	characteristics
Base case			
102 Mg (100 long tons) per day Claus sulfur	Sour water condensate	<0.25 liter/min (0.07 gal/min)	1500-2000 ppm H_2S; 1000 ppm NH_3
Emission control alternatives			
Oxidation/scrubbing processes			
Wellman-Lord	Sour water condensate	20 liters/min (5.3 gal/min)	pH ~2
	Scrubbing solution purge	15 liters/min (4.0 gal/min)	25% sodium salts; 75% water
IFP-1500	Sour water condensate	20 liters/min (5.3 gal/min)	pH ~2
	Catalyst wash	~28,000 liters/2 yr (7400 gal/2 yr)	
Reduction/scrubbing process			
Beavon	Sour water condensate	45 liters/min (12 gal/min)	50 ppm H_2S; trace NH_3
	Scrubbing solution purge	5 liters/min (1.3 gal/min)	2% sodium salts; 98% water
SCOT	Sour water condensate	45 liters/min (12 gal/min)	50 ppm H_2S; trace NH_3

refinery sulfur plants. Furthermore, other than those resources initially required to construct the emission control system (most of which could probably be salvaged in one way or another), there does not appear to be any irreversible or irretrievable commitment of resources associated with these systems. There is even no overall increase in the energy requirements associated with refinery sulfur plants, because the emission control systems result in a net reduction in energy consumption.

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5.4 NATURAL GAS INDUSTRY

Natural gas often contains hydrocarbon condensates (such as natural gasoline, butane, and propane) and water. These condensates are usually removed at a field separator located near the well site (see Figure 5.4-1).[1] Natural gas from some reservoir formations contains such acid gases as gaseous sulfur compounds and carbon dioxide (CO_2). Approximately 95 percent of U.S. natural gas production is free of sulfur compounds and is referred to as sweet.[2] Natural gas containing sulfur compounds is referred to as sour. Sour natural gas contains hydrogen sulfide (H_2S) in widely varying concentrations, together with trace amounts of organic sulfur compounds such as mercaptans (RSH), carbonyl sulfide (COS), and carbon disulfide (CS_2). Hydrogen sulfide rarely constitutes less than 95 percent of the total sulfur content.[3] To meet pipeline gas specifications of 6 mg H_2S per standard cubic meter (0.25 gr/100 std ft^3) and heat content of 37 MJ/std m^3 (1000 Btu/std ft^3), and to obtain fuel gas of low sulfur content for plant use, the processors "sweeten" the sour natural gas; i.e., they remove the "acid gases."

Sour natural gas is processed in 17 states ranging from Michigan and Ohio to California and from North Dakota to Texas and Florida. Capacities of the processing plants range from less than 27×10^6 std m^3/yr (1×10^9 std ft^3/yr) to 4×10^9 std m^3/yr (148×10^9 std ft^3/yr) of sour gas processed. Quantities of sulfur available in the sour gas range from less than 1000 Mg/yr (1000 long tons/yr) to 155,000 Mg/yr (153,000 long tons/yr).[4] There is a general trend to larger plants as the production of groups of wells is consolidated for processing in individual plants. The size of a plant, however, is dictated by the amount of well production in an area the plant can feasibly serve. Therefore, new plants are likely to cover a considerable size range.

Emissions from gas treating plants may include unrecovered sulfur compounds (H_2S, COS, and CS_2), SO_2 (from oxidation of sulfur compounds), and CO.

5.4.1 Major Natural Gas Desulfurization Processes

Gas sweetening processes can be grouped into four major categories: 1) amine and amine-type processes; 2) carbonate and other chemical proc-

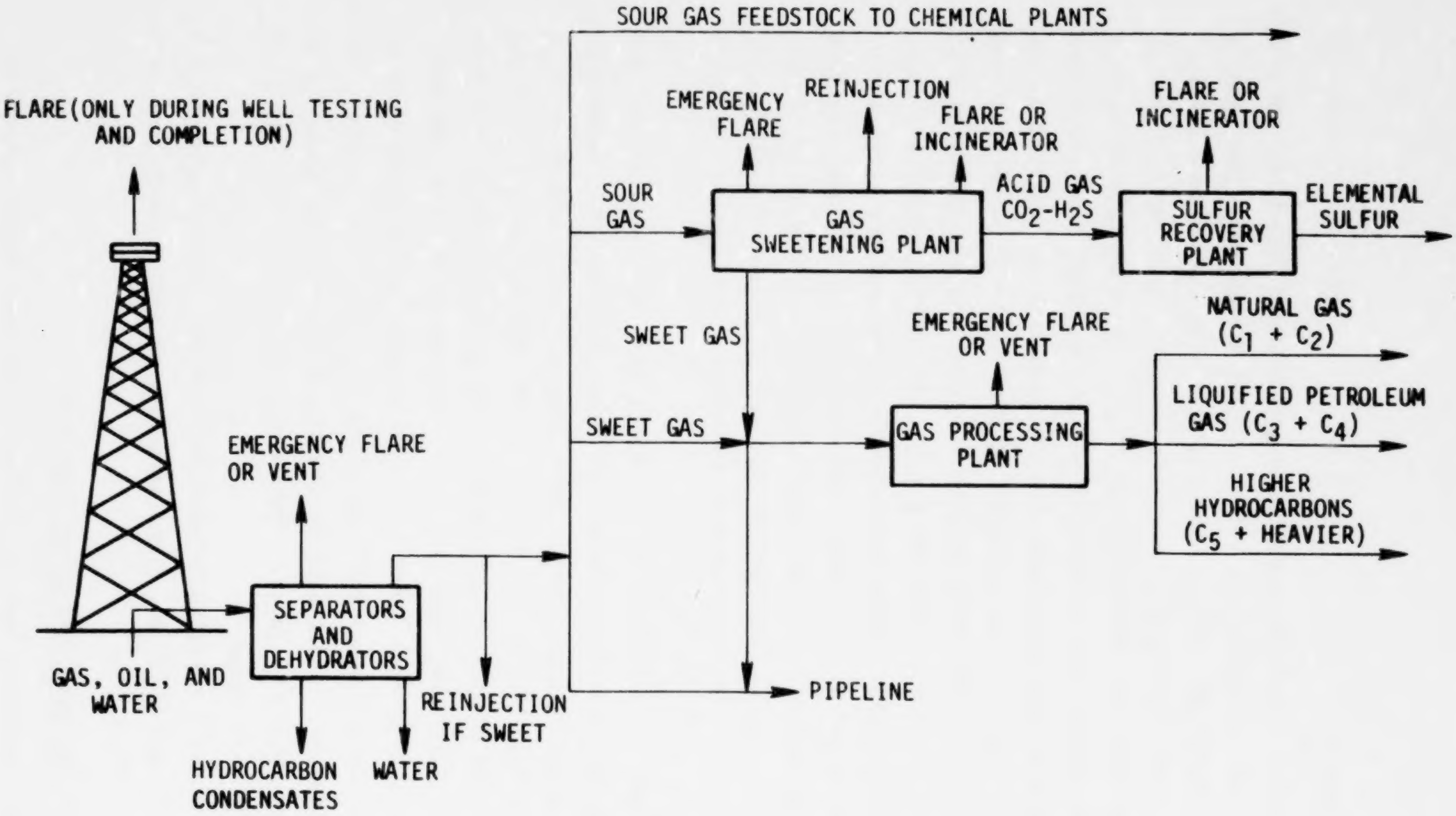
FLARE(ONLY DURING WELL TESTING AND COMPLETION)
GAS, OIL, AND WATER
EMERGENCY FLARE OR VENT
SEPARATORS AND DEHYDRATORS
HYDROCARBON CONDENSATES
WATER
REINJECTION IF SWEET
SOUR GAS FEEDSTOCK TO CHEMICAL PLANTS
SOUR GAS
EMERGENCY FLARE
REINJECTION
FLARE OR INCINERATOR
GAS SWEETENING PLANT
ACID GAS CO_2-H_2S
FLARE OR INCINERATOR
SULFUR RECOVERY PLANT
ELEMENTAL SULFUR
SWEET GAS
SWEET GAS
EMERGENCY FLARE OR VENT
GAS PROCESSING PLANT
NATURAL GAS (C_1 + C_2)
LIQUIFIED PETROLEUM GAS (C_3 + C_4)
HIGHER HYDROCARBONS (C_5 + HEAVIER)
PIPELINE

Figure 5.4-1. Generalized flow diagram of natural gas processing.[1]

esses; 3) physical absorption processes, and 4) solid bed sweetening processes. This section will only discuss the amine processes since they are used for over 95 percent of all gas sweetening in the United States.[5]

Sulfur in acid gases not present in sufficient quantities to be recovered may be vented, flared, or incinerated. When there are sufficient quantities of sulfur, acid gas from the sweetening processes goes to a sulfur recovery system, which in most cases consists of a Claus-type plant. The system may include equipment for treating the Claus tail gas.

In the amine process (also known as the Girbotol process and invented by Girdler) various amine solutions are used as absorbents for H_2S. Amine processes were developed to remove high concentrations of H_2S and CO_2 in large volumes of gas. Pressures may be as low as 240 kPa (35 psig). The alkanolamines are the most generally accepted and widely used of the many available solvents for removal of H_2S and CO_2. The three alkanolamines generally used in gas sweetening are monoethanolamine (MEA), diethanolamine (DEA), and triethanolamine (TEA). Of these three, MEA is usually preferred.

The basic amine process is summarized in the following reaction:

$$2\ RNH_2 + H_2S \rightarrow (RNH_3)_2\ S$$

where:
R = mono-, di-, or triethanol
N = nitrogen
H = hydrogen
S = sulfur

The basic amine process system is illustrated in Figure 5.4-2.

The hydrocarbon gas (sour gas) enters the bottom of the absorber. The lean amine solution (RNH_2) contacts the gas countercurrently in a tray or packed tower and absorbs the H_2S and some of the other acid impurities contained in the gas. The lean amine solution at normal temperatures of 21° to 49°C (70° to 120°F) forms a compound with H_2S. The desulfurized gas leaves the top of the absorber, while the rich amine solution is sent to the regenerator column. In the regenerator, the volatile H_2S and CO_2 are

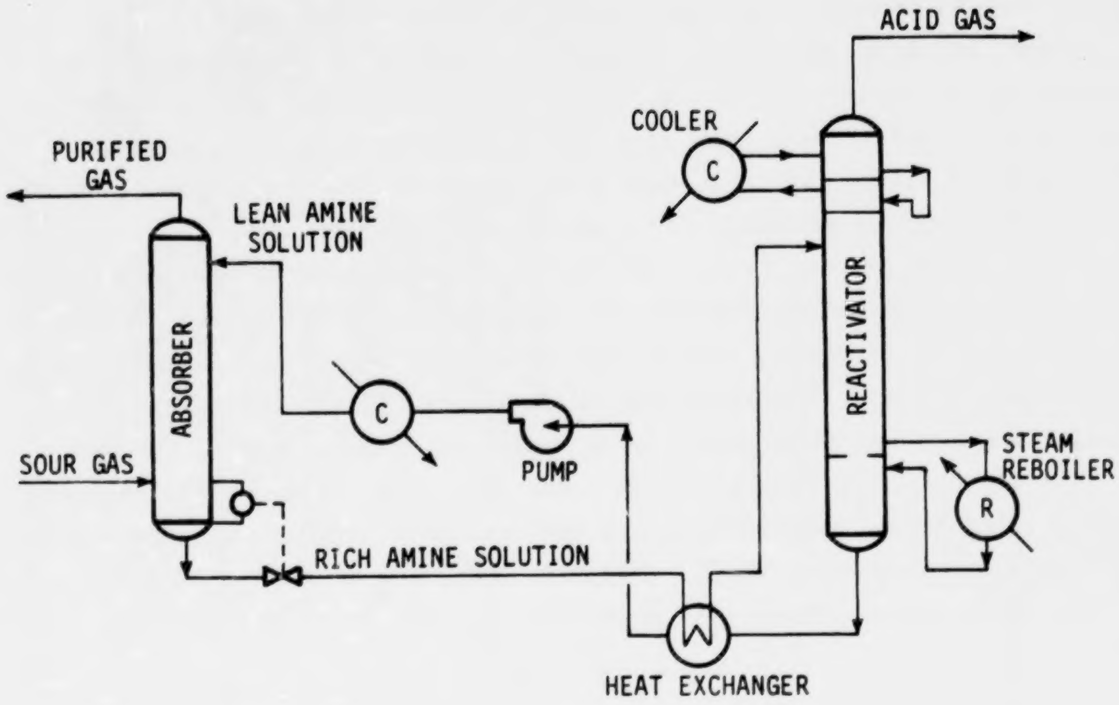
ACID GAS
COOLER
C
PURIFIED GAS
LEAN AMINE SOLUTION
ABSORBER
C
REACTIVATOR
SOUR GAS
PUMP
STEAM REBOILER
R
RICH AMINE SOLUTION
HEAT EXCHANGER

Figure 5.4-2. Flow diagram of the amine process for gas sweetening.

separated from the relatively nonvolatile amine by steam stripping. The regenerated (lean) amine solution is cooled and sent to the amine storage tank for eventual return to the absorber. The acid gas stream from the regenerator is cooled and then sent to the sulfur plant.

Small quantities of H_2S are flared. When present in recoverable quantities, sulfur is usually removed from the acid gas by means of a Claus type sulfur recovery system whereby exothermic oxidation reactions convert H_2S to elemental sulfur. The basic Claus reactions are

$$H_2S + 1/2\ O_2 \rightarrow H_2O + S$$

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O$$

$$2\ H_2S + SO_2 \rightarrow 3S + 2\ H_2O$$

Four major variations of the Claus system are as follows:

1) Straight-through Claus--used where acid gas contains 50 to 100 percent H_2S.

2) Split-flow Claus--used where acid gas contains 15 to 50 percent H_2S.

3) Direct-oxidation Claus--used where acid gas contains 2 to 15 percent H_2S.

4) Sulfur-recycle Claus--also used where acid gas contains 2 to 15 percent H_2S.

The straight-through Claus system is the one generally found in petroleum refineries. The acid gas concentration is high enough for combustion to occur when the acid gas is mixed with the quantity of air optimum for oxidizing the H_2S to elemental sulfur. A complete discussion of this Claus system is contained in Section 5.3.1.7.

The split-flow Claus process is the primary system used in sour gas processing plants because of the lower H_2S concentration. One-third of the acid gas flow and the process air are introduced to the combustion chamber where they react. The remaining acid gas stream is injected into the combustion chamber bypassing the burners and mixed with the combustion gases for the Claus reaction to occur. Typically, the process gases leave the combustion chamber and enter first a waste heat boiler and then a condenser followed by a reheater before the catalytic reactor. After passing through the reactor where H_2S and SO_2 react to form sulfur and water, the gases again flow to a sulfur condenser. The gas must be reheated and sent through additional catalytic stages to increase the sulfur yield and overall plant efficiency.

A variation of the split-flow Claus-type process with process gas and combustion air preheat is used when the H_2S concentration is not high enough to support combustion. The acid gas and the process air are preheated by heat exchange with process gas from the combustion chamber or in direct-fired heaters. Adequate acid gas and air preheat is essential to maintaining a stable gas flame in the reactor furnace. Again, approximately one-third of the acid gas flow and the process air are introduced to the combustion chamber, and the remaining acid gas stream is injected into the chamber bypassing the burners. Because the heat of reaction in the formation of SO_2 is about four-fifths of the total heat of reaction in the conversion of H_2S to sulfur, a waste heat boiler is used to produce process steam. A reactor-condenser train with process gas reheat prior to each reactor follows the waste heat boiler.

There is no Claus combustion chamber in the direct-oxidation or catalytic process. The acid gas is heated, mixed with air and SO_2, and passed directly to a catalytic reactor. The SO_2 needed for catalytic conversion is generated in a sulfur combustion chamber with the addition of the necessary combustion air. Two or three reactors are commonly used in this process.

In the sulfur-recycle process, product sulfur is recycled to the combustion chamber. The quantity of sulfur burned is limited to maintain the H_2S to SO_2 ratio of 2:1. The SO_2 formed and the H_2S in the acid gas feed undergo combustion according to the Claus reaction. A reactor-condenser train similar to those previously described follows the combustion chamber.

The direct-oxidation and sulfur recycle Claus processes are not generally used. It is possible to use a split-flow Claus unit to process acid gas streams with very low H_2S concentrations (2 to 15 percent) if supplemental fuel gas is added to insure combustion of the H_2S.[6,7] It may not be possible, however, to produce a salable product in this case because of color and/or carbon content added by the supplemental fuel combustion.

Acid gases obtained from natural-gas sweetening processes vary greatly in H_2S content and may contain impurities such as CO_2, hydrocarbons, and water vapor. (Ammonia is normally only found in refinery acid gas.) These feed gas impurities create costly and troublesome problems affecting design, maintenance, and operation of a Claus sulfur plant. The major problem is reduced sulfur conversion because of the effect of dilution by inerts.

Excessive CO_2 in the feed increases sulfur emissions to the atmosphere because of the formation of COS and CS_2, which exits with the tail gas.[8] The CO_2 acts as the main inert, instead of requiring large quantities of additional combustion air. Excessive hydrocarbons in the feed also increase sulfur emissions because of the formation of COS and CS_2. Additional combustion air is required for oxidation of the hydrocarbons forming CO_2 and water vapor. There is also a corresponding increase in waste heat boiler duty due primarily to the additional heat release from combustion of the hydrocarbons. Water vapor acts as a true inert, as well as being a product of the Claus reaction. Therefore, both the equilibrium of the Claus reaction and the effective partial pressures of the reactants are affected.[8] Factors also influencing sulfur plant efficiency are changes in the ratio of H_2S to CO_2 and the acid gas rate, which may occur because of changes in the production of the gas field.[8]

If the acid gas stream contains excessive amounts of these impurities, several alternatives should be studied to enrich the stream with respect to H_2S. Several absorption processes that are selective for H_2S in the presence of CO_2 are available. Charcoal adsorption units can be considered for removing hydrocarbons from acid gases prior to sending the gas to the Claus unit. Water vapor can be condensed and separated from the acid gas stream.[8]

The water formed in the Claus reaction is emitted as vapor and is not an emission problem. There is some sour water generated by overflow from the absorber that may contain both sulfur compounds and spent amine. The volume is small, but some form of treatment prior to disposal may be appropriate. This stream can be corrosive to metal insufficiently protected.

The tail gas from the sulfur recovery unit is a major sulfur source in a natural-gas sweetening plant and usually requires SO_2 control. Air quality control restrictions normally require the use of a Claus-tail gas treating unit for further reduction of SO_2 emissions.[9]

5.4.2 Control Techniques

Operational tail-gas control systems include the IFP-1500 process, the SCOT system, the Sulfreen process, the Beavon process, the Stretford process, and the Wellman-Lord process. These tail-gas control systems have been described in detail in Section 5.3.2.1 of this document.

5.4.2.1 Control Cost--

Sour gas processing operations include a natural gas treater (usually an amine absorption process) and a sulfur recovery system. Table 5.4-1 shows the capital and operating costs for two sizes of amine units. Cost estimates for amine units will vary with location, gas pressure, H_2S content, CO_2 content, and nitrogen content.

The hydrogen sulfide content in the natural and acid gas stream is the predominant cost parameter of sulfur recovery plants. The volume of CO_2 in the source stream is also significant in costing sulfur recovery plants. An acid gas stream with 50 percent CO_2 will require equipment that is twice as large as a 100 percent H_2S acid gas stream to maintain a constant flow rate for the same sulfur capacity. Efficiency of the catalyst decreases with dilution, and larger beds are required.

Other investment costs developed for the natural-gas processing industry show the effect of low H_2S concentrations on sulfur recovery plant capital costs. As can be seen from Figure 5.4-3, the cost of a 100-Mg/day (100-long-ton/day) two-stage sulfur recovery plant more than doubles when processing an acid gas containing 15 percent H_2S versus an acid gas containing 90 percent H_2S.[11]

Legislation requiring the reduction of SO_2 emissions from sulfur recovery units may necessitate the addition of tail-gas treating units. The cost of recovering this incremental sulfur is high and is approximately 90 percent of the cost of a new Claus unit.[10] Capital and operating costs for tail-gas treating units are discussed in Section 5.3.2.2. The costs are based on a typical refinery acid gas stream in excess of 70 percent H_2S.

TABLE 5.4-1. TYPICAL AMINE UNITS COSTS
(Mid-1979 dollars)

	Plant capacity	
	0.57 M m^3/day (20 x 10^6 ft^3/day)	2.27 M m^3/day (80 x 10^6 ft^3/day)
Investment:		
(1) Plant cost	$2,160,000	$8,650,000
(2) Working capital, 15% of (1)	324,000	1,300,000
(3) Total capital cost	2,484,000[a]	9,950,000[a]
Operating costs:		
(4) Capital recovery cost, 18% of (3)	$ 447,000	$1,790,000
(5) Taxes and insurance, 3% of (1)	65,000	260,000
(6) Total fixed costs, (4) + (5)	512,000	2,050,000
(7) Operating labor	108,000	108,000
(8) Maintenance, 4% of (1)	86,000	346,000
(9) Supplies	15,000	60,000
(10) Utilities	646,000	2,856,000
(11) Chemicals	124,000	497,000
(12) Total direct costs, (7) + (8) + (9) + (10) + (11)	979,000	3,597,000
(13) Total operating cost, (6) + (12)	1,491,000	5,647,000

[a] Reference 10 used to estimate total capital cost. Other costs are based on engineering judgement.

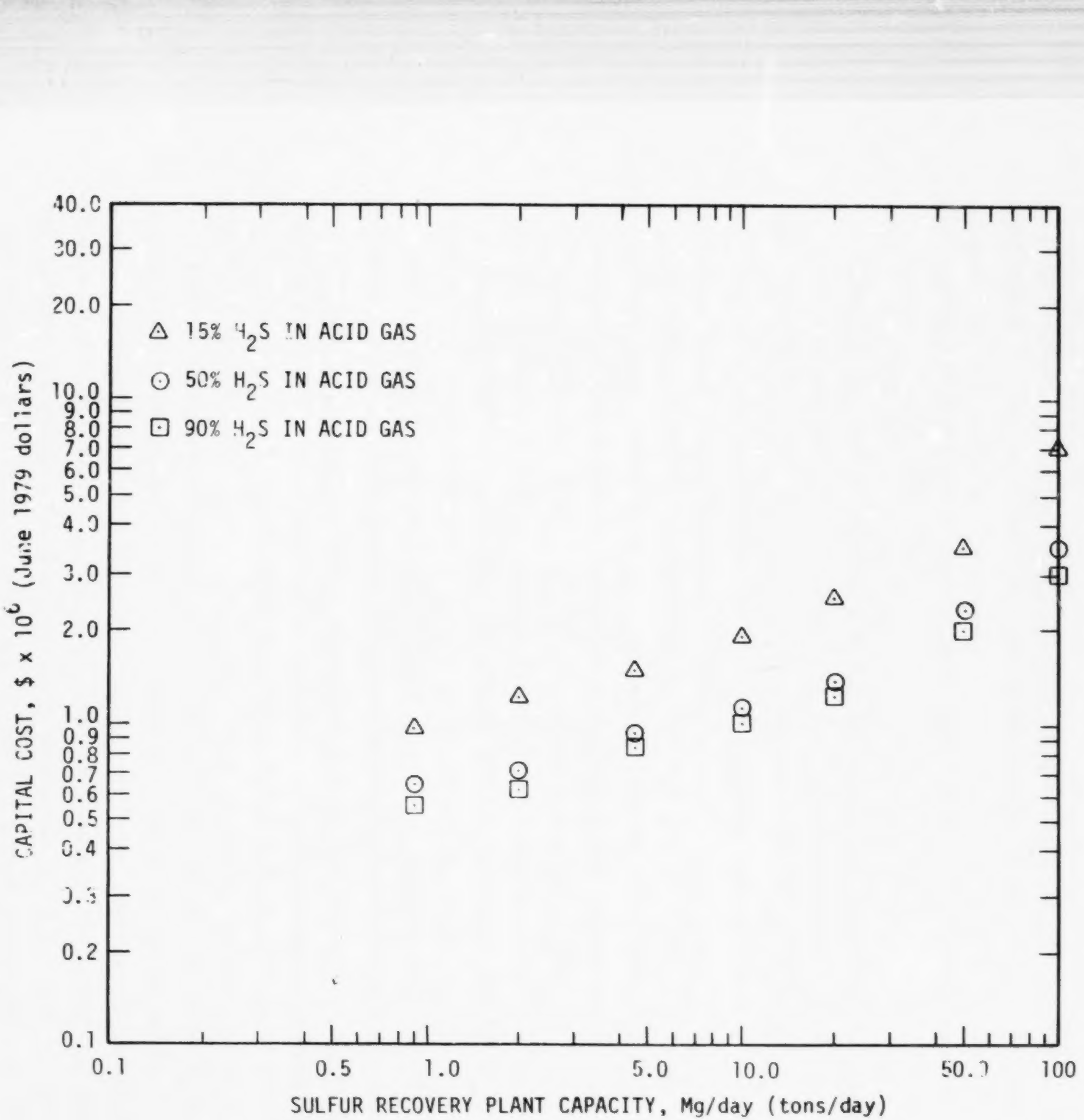

Figure 5.4-3. Capital cost of Claus (two-stage) plus incinerator.[11]

The effects on the cost of tail-gas treating units for acid gases with reduced hydrogen sulfide concentrations are similar to those discussed above for sulfur plants.

5.4.2.2 Energy and Environmental Impact--

The energy requirements and environmental impact for tail-gas treating units are discussed in Section 5.3.2.3. The costs are based on a typical refinery acid gas stream. Energy requirements will be increased for tail-gas treating units when the H_2S concentration of the acid gas is low because of larger processing equipment needed to handle the increased gas flow rate.

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11. Ref. 2, p. 8-40.

5.5 SULFURIC ACID PLANTS

Sulfuric acid, the most important mineral acid, is the most widely used industrial chemical. The chief uses of sulfuric acid are in production of fertilizer, manufacture of chemicals, oil refining, pigment production, iron and steel processing, synthetic fiber production, and metallurgical operations. Sulfuric acid production in 1975 was 29.3 Tg (32.3 million tons) from a total of about 150 plants.[1] Florida has the greatest number of acid plants (20), followed by New Jersey (9); Virginia (8); and Louisiana, North Carolina, and California (6 each). The basic processes used for the production of sulfuric acid are the contact process and the chamber process. The latter accounts for only 0.3 percent of the total production, however, and no new chamber process plants are being built. Further, the older chamber plants are being phased out. The entire discussion in this section is focused on the contact process.

Sulfuric acid is produced by burning sulfur or sulfur-bearing materials to form SO_2. Sources of SO_2 include 1) elemental sulfur, 2) spent acid, 3) smelter off-gas, 4) pyrites, and 5) waste gas from fossil-fuel-fired boilers. Table 5.5-1 lists the capacity and the percentage of total capacity of the major sulfuric acid manufacturing sources in the United States for the years 1976 to 1980. The average operating rate, which determines the actual production, reached a peak of almost 90 percent of capacity during 1973-1974. In 1975, the average operating rate dropped to only 67 percent of capacity.

5.5.1 Process Descriptions and Emission Sources

Contact sulfuric acid plants are classified as hot gas (sulfur burning) or cold gas (metallurgical and spent acid) systems. Plants operating on elemental sulfur receive hot SO_2 gas directly from the sulfur burner and waste heat recovery system. When SO_2 gas from a metallurgical operation or other byproduct source (such as spent acid or iron pyrites) is used, it is received cold from the wet scrubber-cooler and purification systems.

A basic variation of the contact process is the double absorption technique, also known as double catalysis. Because use of this design is largely based on the need to meet air pollution control regulations, it is discussed under Section 5.5.2, Control Techniques.

TABLE 5.5-1. U.S. SULFURIC ACID CAPACITY[1]

[Tg/yr (millions of tons/yr) of 100% H_2SO_4]

Source	1976		1977		1978		1979		1980	
	Capacity	Percent of total	Capacity	Percent of total	Capacity	Percent of total	Capacity	Percent of total	Capacity	Percent of total
Contact process										
Sulfur burning	27.48 (30.29)	68.8	28.18 (31.06)	68.8	28.22 (31.11)	68.4	28.85 (31.80)	68.9	28.84 (31.79)	68.7
Spent acid	6.91 (7.62)	17.3	6.91 (7.62)	16.9	6.91 (7.62)	16.8	6.91 (7.62)	16.5	6.91 (7.62)	16.5
Smelter off-gas	5.49 (6.05)	13.8	5.79 (6.38)	14.2	6.07 (6.69)	14.7	6.07 (6.69)	14.5	6.17 (6.80)	14.7
Chamber process	0.05 (0.06)	0.1	0.05 (0.06)	0.1	0.05 (0.06)	0.1	0.05 (0.06)	0.1	0.05 (0.06)	0.1
Total	39.93 (44.02)	100.0	40.93 (45.12)	100.0	41.26 (45.48)	100.0	41.88 (46.17)	100.0	41.97 (46.27)	100.0

5.5.1.1 Sulfur Burning Plants[2]--

In sulfur burning contact plants, shown schematically in Figure 5.5-1, sulfur is melted and filtered to remove traces of ash. The molten sulfur is atomized and burned with dry combustion air in the following reaction:

$$S_{(l)} + O_{2(g)} \rightarrow SO_{2(g)} \qquad \Delta H = -0.297 \text{ kJ/kg-mol at } 25°C\ (77°F)$$

The excess heat of combustion of sulfur is utilized in a waste heat boiler to generate steam for melting the sulfur and in other process areas. Normally the amount of steam produced, by weight, is greater than the amount of 100 percent sulfuric acid produced.[2] The hot gas (7 to 12 percent SO_2, 9 to 13 percent O_2) is filtered and passed through a catalytic converter (platinum mass units or units containing beds of pelletized vanadium pentoxide) to oxidize SO_2 to SO_3 by the following reaction:

$$SO_{2(g)} + 1/2\ O_{2(g)} \rightleftarrows SO_{3(g)} \qquad \Delta H = -0.098 \text{ kJ/kg-mol}$$

The exothermic, reversible oxidation of SO_2 involves an inherent conflict between the high equilibrium conversions at lower temperatures and the favorable reaction rates at higher temperatures. Plant operators attempt to optimize the process by first passing the combustion gas over a part of the catalyst at about 420°C (788°F) where the reaction rate is high until about 70 to 75 percent of the SO_2 is converted, with a consequent rise in temperature to around 600°C (1112°F), where equilibrium is approached. The gas is then cooled in a heat exchanger to about 430°C (806°F) and passes over two or three more catalyst stages with intermediate cooling. The conversion of SO_2 to SO_3 is about 97 to 98 percent.

The gas leaving the converter is cooled in an economizer, with additional cooling sometimes obtained by air-cooled heat exchangers. The SO_3 is absorbed in a stream of strong (98 to 99.5 percent) acid. The SO_3 reacts with the water in the acid to form additional sulfuric acid. Dilute sulfuric acid or water is in turn added to the recirculating acid to maintain the desired concentration. If oleum (fuming sulfuric acid) is produced, the economizer exit gases are passed through an oleum tower, which is fed with the strong acid from the absorption tower.

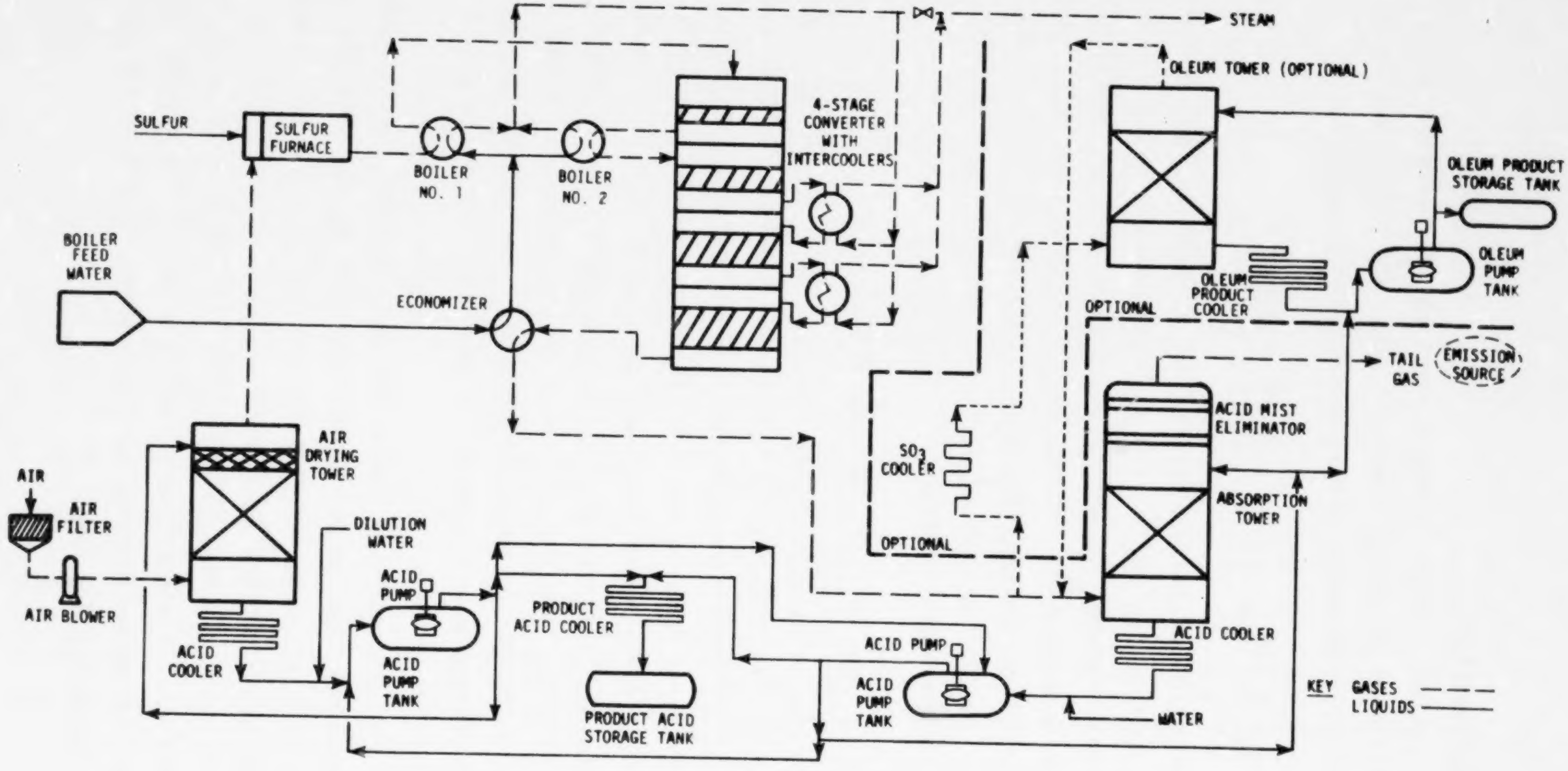

STEAM
SULFUR
SULFUR FURNACE
BOILER NO. 1
BOILER NO. 2
4-STAGE CONVERTER WITH INTERCOOLERS
OLEUM TOWER (OPTIONAL)
OLEUM PRODUCT STORAGE TANK
BOILER FEED WATER
ECONOMIZER
OLEUM PRODUCT COOLER
OLEUM PUMP TANK
OPTIONAL
TAIL GAS
EMISSION SOURCE
SO_3 COOLER
ACID MIST ELIMINATOR
AIR DRYING TOWER
ABSORPTION TOWER
AIR
AIR FILTER
DILUTION WATER
OPTIONAL
ACID PUMP
AIR BLOWER
PRODUCT ACID COOLER
ACID COOLER
ACID COOLER
ACID PUMP
ACID COOLER
ACID PUMP TANK
ACID PUMP TANK
PRODUCT ACID STORAGE TANK
WATER
KEY GASES
LIQUIDS

Figure 5.5-1. Flow diagram of a single-absorption, contact-process plant that produces sulfuric acid by burning sulfur.[a]

5.5.1.2 Cold Gas Plants[2]--

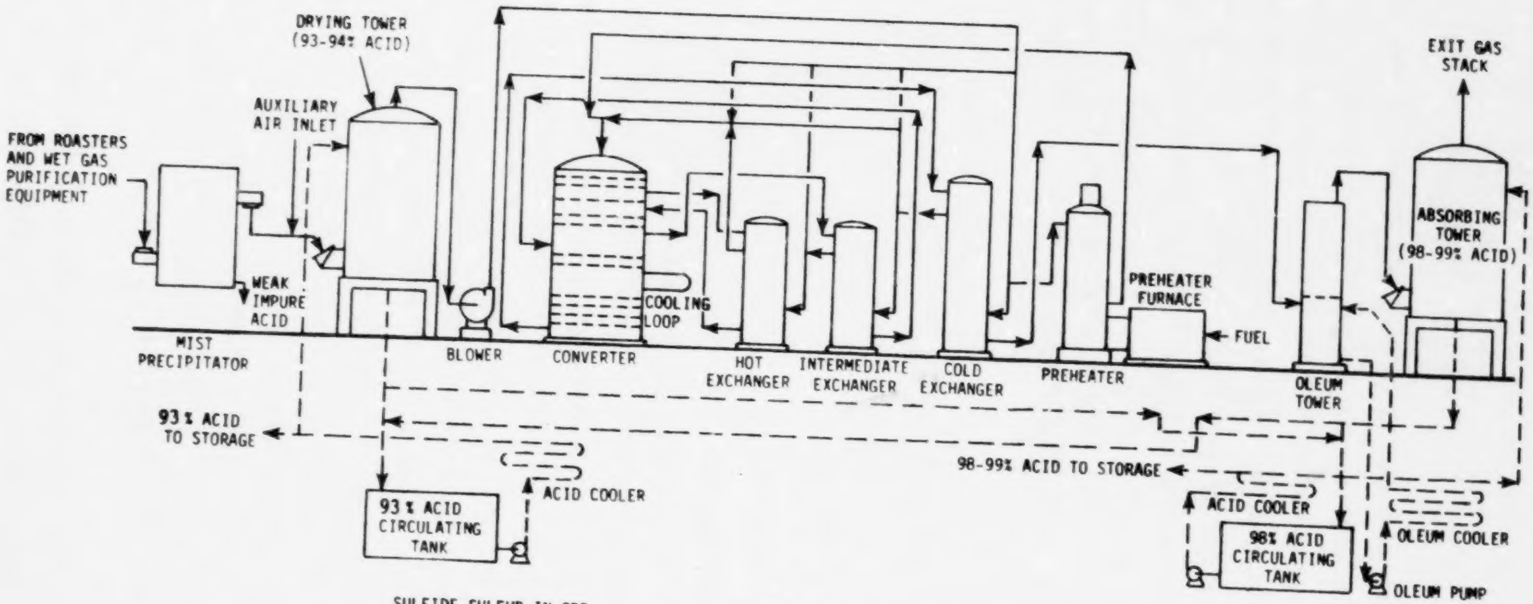
Cold gas sulfuric acid plants use raw materials other than elemental sulfur. The typical raw materials are sulfide ores, spent or sludge acid, or waste gas from metallurgical operations. The cold gas processes require extensive gas pretreatment involving dust removal, cooling, and scrubbing for further removal of particulate matter and heavy metals, mist, and moisture. When gas streams contain less than 10 percent SO_2, the size of the equipment required to produce a given quantity of acid is relatively greater because higher gas volumes are required. The capital and operating costs for a cold gas plant are therefore much higher than those for a corresponding sulfur-burning acid plant.

The process configuration of a cold gas plant depends upon the source of the SO_2. Figure 5.5-2 shows the overall flow diagram for a cold gas sulfuric acid process applicable to ore-roasting plants and spent acid regeneration plants.[2]

5.5.1.3 Sulfur Dioxide Emissions--

Normal operations--Figure 5.5-3 shows the relationship between volumetric and mass emissions of SO_2 and conversion efficiency at various concentrations of SO_2 at the converter inlet.[4] Although it is necessary to provide adequate residence time for the reacting gases in the catalyst mass, the conversion efficiency of the contact process is more directly affected by the effectiveness of interstage cooling. The conversion is also inversely related to the SO_2 concentration of incoming gases. The converter unit consists of three, four, or five fixed beds of catalyst with interstage cooling to maintain the optimum gas reaction temperature-conversion profile. Plants built before 1960 generally had only three conversion stages and operated with conversion efficiencies of about 95 to 96 percent.[5] Plants built since 1960 have four or more converter stages and overall conversion efficiencies between 96 and 98 percent.[5] Typical SO_2 emissions from various types of single absorption plants without SO_2 tail gas recovery systems are shown in Table 5.5-2.[6]

Acid mist is also emitted from sulfuric acid plants. The quantity of acid mist formed depends on the strength of acid produced, the type of


FROM ROASTERS AND WET GAS PURIFICATION EQUIPMENT
MIST PRECIPITATOR
WEAK IMPURE ACID
AUXILIARY AIR INLET
DRYING TOWER (93-94% ACID)
BLOWER
CONVERTER
COOLING LOOP
HOT EXCHANGER
INTERMEDIATE EXCHANGER
COLD EXCHANGER
PREHEATER
PREHEATER FURNACE
FUEL
OLEUM TOWER
ABSORBING TOWER (98-99% ACID)
EXIT GAS STACK
93% ACID TO STORAGE
93% ACID CIRCULATING TANK
ACID COOLER
98-99% ACID TO STORAGE
ACID COOLER
98% ACID CIRCULATING TANK
OLEUM COOLER
OLEUM PUMP

SULFIDE SULFUR IN ORE	316 kg	PER Mg 100% ACID IN PLANT OF 200 Mg DAILY CAPACITY (VALUES DEPENDENT ON TYPE OF ORE AND ROASTER)
WATER	7.326 m^3	
ELECTRICITY	50 kwh	
DIRECT OPERATING LABOR	0.72 man-h	
STEAM CREDIT	725 kg	

INVESTMENT: 2 1/2 TIMES THAT FOR SULFUR-BURNING PLANT INCLUDING ROASTERS AND GAS PURIFIERS

Figure 5.5-2. Flow diagram for ore-roasting contact plant.[2]

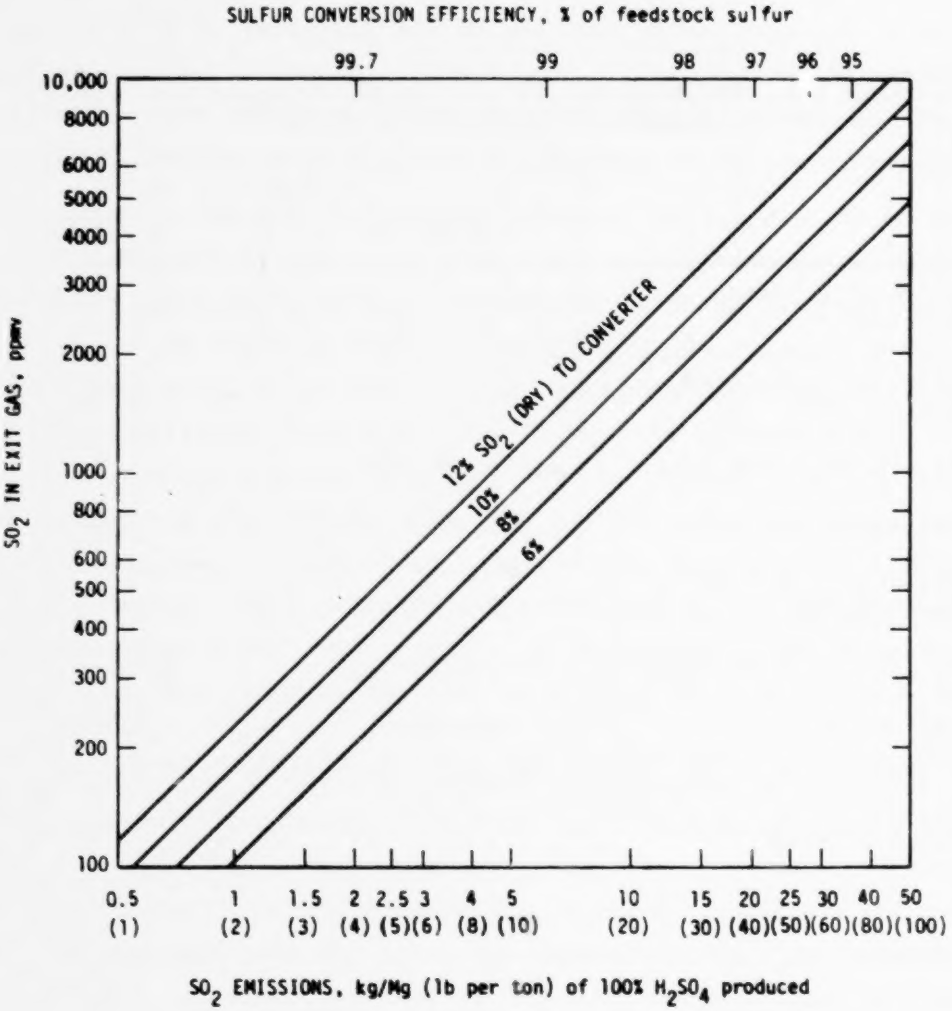


Figure 5.5-3. Volumetric and mass SO_2 emissions from contact sulfuric acid plants.[4]

TABLE 5.5-2. UNCONTROLLED SULFUR DIOXIDE EMISSIONS FROM SINGLE ABSORPTION SULFURIC ACID PLANTS[6]

	Feedstock	
	Sulfur	Acid sludge
SO_2 in converter feed, % by volume	7.5-8.8	6-8
SO_2 emissions from three stage converter,		
kg/Mg (lb/ton) 100% acid	28-35 (56-70)	NA
ppm by volume	3000-5000	NA
SO_2 emissions from four-stage converter		
kg/Mg (lb/ton) 100% acid	13-28 (26-56)	15-56 (30-112)
ppm by volume	1500-4000	1500-4000

NA - Not available.

sulfur feedstock, and the absorption efficiency. The acid mist is controlled by high-efficiency vertical tube mist eliminators. Details on acid mist control technology are published.[7]

Sulfur dioxide emissions may exceed the normal emission rate during startup or abnormal operations. The frequency and duration of the abnormal emissions depend on the plant design, type of control systems, and the nature of the startup or operational problem.

Startup--The amount of SO_2 emitted during startup depends on the time needed to bring all of the converter stages to the proper operating temperatures. Time required to achieve a stable operation of the plant depends on the length of the shutdown and the condition of the catalyst bed. When a plant has been charged with new catalyst, a startup will require 1 to 2 days of slowly increasing production rates until full production is reached. Plants with catalyst exposed to moisture can be in full production in 3 to 4 days. During startup, the emissions may be five times the normal rate for the first few hours if the final stage is not at the proper temperature before SO_2 is introduced into the converter. If the preceding stages are sufficiently heated to obtain nearly full conversion at reduced rates, reaction heat then continues the heating process until ignition is obtained in the final bed.

Upon completion of the preheating sequence, sulfur or sulfur-containing feedstock is burned at a low rate with excess air to produce a weak SO_2 stream, which is fed to the converter. Adjustments are made to stabilize all operations, bringing all temperatures to normal conditions and gradually increasing the feed rate and inlet SO_2 concentration as the temperature of the first bed decreases and that of the last bed increases to ignition. These adjustments must be carefully coordinated to prevent loss of stability and resultant excessive SO_2 emissions.

Abnormal operation--During routine operation several types of abnormal conditions can cause excessive emissions. Elemental-sulfur-burning plants have the fewest problems because they operate with a relatively constant concentration of SO_2 to the converter. Plants using spent acid or some of the various metallurgical off-gases are more prone to operating problems, the most common of which are listed below:

1. Sudden change in concentration of SO_2 to the converter; occurs in plants using spent acid or metallurgical off-gases as feed.

2. Oxygen starvation; occurs in plants using roaster gas as feed.

3. Equipment failure or power failure.

Emissions during these conditions usually range from 50 to 100 percent higher than normal levels. Usually, the operations are stabilized within a few hours.

5.5.2 Control Techniques

Technology for control of SO_2 emissions from sulfuric acid plants is well established. The double absorption process is operating successfully at over 200 plants throughout the world, including 40 plants in the United States. In addition, several desulfurization processes are applicable to tail gases from a sulfuric acid plant. These processes, which could be applied to all classes of contact acid plants when operated with a high-efficiency Brink-type mist eliminator in the final absorbing tower, provide simultaneous control of SO_2, SO_3, and acid mist. The two processes with maximum potential for controlling SO_2 emissions from acid plants are sodium sulfite (Wellman-Lord) and ammonia scrubbing. These processes and others that may also be applicable to sulfuric acid plants are discussed in Section 4.2.3. The discussion here is limited to a brief review of the processes currently in operation on acid plants in the United States.

The size of an emission control system for tail gas is decided by the flow rate of the exhaust gas to be handled. The exhaust gas flow rate at an acid plant is a near linear function of the daily production rate. The relationship between exhaust gas flow rate and daily production rate is shown by the following equation:[8]

$$\text{Exhaust gas flow, Nm}^3\text{/s} = 0.0357 \times \text{daily production rate in megagrams/day} - 1.31$$

$$(\text{Exhaust gas flow, 1000 scfm} = 0.074 \times \text{daily production in tons/day} - 3.0)$$

This relationship applies to sulfur-burning contact acid plants with SO_2 concentrations at the converter inlet of 10 percent. For cold gas plants, which have much lower SO_2 concentrations, the exhaust gas flow will be correspondingly higher for a given production rate.

5.5.2.1 Description--

Double absorption--The sulfur combustion portions of the single and double absorption plants are similar. Combustion air is dried in a tower with 93 to 98 percent sulfuric acid before being introduced in the sulfur furnace. Furnaces normally operate with gas strengths of 9 to 12 percent SO_2.

Using a double absorption process, a plant can convert 99.7 to 99.8 percent of the SO_2 produced to SO_3. The primary difference between the single and double absorption processes is the addition of a primary SO_3 absorber for gas leaving the third catalyst bed.[9] Some processes use this absorber after the second bed. In the primary absorption tower the concentration of SO_3 in the gas is reduced to approximately 100 ppm by contact with 98.5 percent sulfuric acid. The gas stream is cooled before the interstage absorber and is reheated before it goes to the next catalyst bed. The type and arrangement of heat exchangers varies, but this cooling and reheating operation is included in all designs.

Approximately 97 percent of the SO_2 remaining in the gas stream is coverted to SO_3 in the fourth catalyst bed. The lower partial pressure of SO_3 drives the reaction to a higher overall conversion rate than is possible in a single absorption plant

The gases leaving the fourth catalyst bed are cooled in a second heat exchanger. The cooled gas passes to a secondary absorption tower containing 98.5 percent sulfuric acid. The gases leaving the secondary absorption tower will contain about 100 to 300 ppm SO_2.

With the exception of the primary absorber and arrangement of the heat exchangers, all major designs of dual absorption sulfuric plants use similar equipment configurations. Design variations are found in converters, heat exchangers, and absorbers.

The double absorption process has proved to be the SO_2 control system of choice for the sulfuric acid industry since the promulgation of NSPS. Of the 32 new units built since the promulgation of NSPS, 28 use the double absorption process for SO_2 control.[10]

Figure 5.5-4 is a flow diagram of the double absorption process;[11] Table 5.5-3 summarizes the status of double absorption processes in the United States as of December 1977.[12,13]

Ammonia scrubbing--This process is described in detail in Section 4.2.3.5; only the salient features of its application to sulfuric acid plants are discussed here. The tail gas from an acid plant is at about 85°C (185°F) and contains only traces of moisture. The adiabatic saturation temperature is about 32°C (90°F). At this temperature, the vapor pressure of ammonia and SO_2 are low, and thus the formation of the "blue haze" characteristically associated with ammonia scrubbing is reduced.

The tail gas, containing 2000 to 3000 ppm of SO_2 and 1.5 g/Nm^3 (0.6 gr/scf) of SO_3 and acid mist, is contacted with ammonium bisulfite/sulfite solution in a two-stage absorber. The lower stage is operated at high bisulfite/sulfite ratio and lower pH (5.5) to minimize ammonia consumption; the upper stage is operated at low bisulfite/sulfite ratio and higher pH (6.5) to maximize SO_2 removal. Within bounds, each stage operates independently. The ammonium sulfite/bisulfite bleed solution from the absorber is fed to the acidulation tank, where H_2SO_4 converts the bisulfite/sulfate to ammonium sulfate, evolving equimolar amounts of SO_2. The acidulated liquor is further stripped of dissolved SO_2 in a packed stripper by air. The stripper off-gas is recycled to the acid plant drying tower along with the acidulation tank off-gas. Ammonium sulfate liquor in concentrations of more than 40 percent is withdrawn from the stripper bottoms. The blue haze, which consists of fine particles of ammonium bisulfite/sulfite, is removed from the stack gases by high-efficiency candle-type mist eliminators.

Figure 5.5-5 is a flow diagram of an ammonia scrubbing process;[14] Table 5.5-4 summarizes the status of ammonia scrubbing systems at acid plants in the United States as of December 1977.[12] The table shows that five installations can meet NSPS, four cannot, and no emission data were available on the other four.

Sodium sulfite (Wellman-Lord) scrubbing--Scrubbing with sodium sulfite is described in Section 4.2.3.6. The basic difference in the desulfuriza-

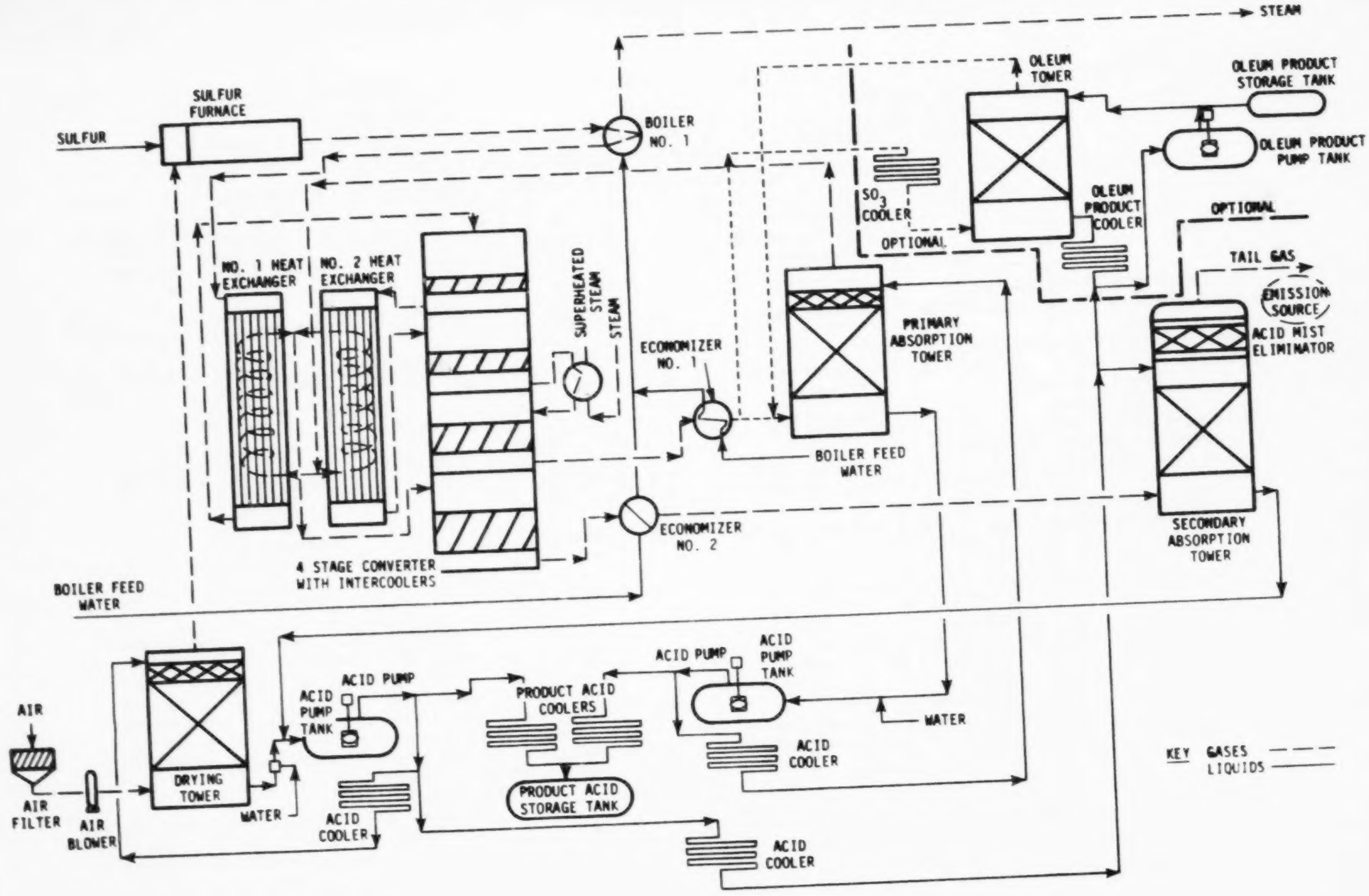

STEAM
SULFUR FURNACE
SULFUR
BOILER NO. 1
OLEUM TOWER
OLEUM PRODUCT STORAGE TANK
OLEUM PRODUCT PUMP TANK
SO_3 COOLER
OPTIONAL
OLEUM PRODUCT COOLER
OPTIONAL
TAIL GAS
EMISSION SOURCE
ACID MIST ELIMINATOR
NO. 1 HEAT EXCHANGER
NO. 2 HEAT EXCHANGER
SUPERHEATED STEAM
STEAM
ECONOMIZER NO. 1
PRIMARY ABSORPTION TOWER
BOILER FEED WATER
ECONOMIZER NO. 2
SECONDARY ABSORPTION TOWER
4 STAGE CONVERTER WITH INTERCOOLERS
BOILER FEED WATER
AIR
AIR FILTER
AIR BLOWER
DRYING TOWER
WATER
ACID PUMP TANK
ACID PUMP
PRODUCT ACID COOLERS
PRODUCT ACID STORAGE TANK
ACID COOLER
ACID PUMP
ACID PUMP TANK
WATER
ACID COOLER
ACID COOLER
KEY GASES
LIQUIDS

Figure 5.5-4. Process flow diagram of a double-absorption, contact-process plant that produces sulfuric acid by burning sulfur.[11]

TABLE 5.5-3. STATUS[a] OF DOUBLE ABSORPTION SYSTEMS ON DOMESTIC SULFURIC ACID PLANTS [10,12,13]

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Agrico Chemical Co.	Bartow, Fla.	2 x 1633 (1800)	Sulfur	N	/75	Parsons	NA	NA	
Allied Chemical Corp.	Anacortes, Wash.	1 x 237 (260)	Sulfur	R	/74	Parsons	NA	1.70[b] (3.41)	
	Claymont, Del.	1 x 907 (1000)	Sulfur	R	9/73	Monsanto	500	3.03 (6.06)	
	Richmond, Calif.	1 x 381 (420)	Sulfur	R	10/74	Parsons	NA	NA	Minor mechanical problems
American Cyanamid	Linden, N.J.	1 x 635 (700)	Sulfur	N	6/70	Monsanto	388	2.36 (4.72)	Interpass heat exchanger replaced because of extensive corrosion
	Savannah, Ga.	1 x 726 (800)	Sulfur	N	4/75	Monsanto	250	1.58 (3.16)	
	Westwego, La.	1 x 1452 (1600)	Sulfur	N	1/78	Monsanto	NA	NA	
American Smelting & Refining Co.	E. Helena, Mont.	1 x 450 (500)	Air-smelter gas	R		Lurgi/ Davy Powergas	NA	NA	
	El Paso, Tex.	1 x 525 (575)	Air-smelter gas	R	12/72	Lurgi/ Davy Powergas	NA	NA	

(continued)

TABLE 5.5-3 (continued)

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Anaconda Co.	Anaconda, Mont.	1 x 600 (660)	Air-smelter gas	R	/72	Lurgi/ Davy Powergas	NA	NA	
Beker Industries	Conda, Idaho	1 x 1560 (1720)	Sulfur	N	3/74	In-house	200	1.21 (2.42)	Booster blower corrosion; absorber tower pump failure
C.F. Industries	Bartow, Fla.	2 x 907 (1000)	Sulfur	R	12/75	Lurgi/ Davy Powergas	600	3.64 (7.28)	Sagging of candles, corrosion in outlet duct of interpass tower
	Bartow, Fla.	2 x 907 (1000)	Sulfur	N	8/75	Monsanto	300	1.82 (3.64)	
	Plant City, Fla.		Sulfur	N	2/75	Monsanto	300	1.82 (3.64)	
Cities Service Co.	Copperhill, Tenn.	1 x 2087 (2300) and 1 x 1542 (1700)	Iron roaster gas	R,N	2/77	Monsanto	NA	NA	
	Lake Charles, La.	1 x 370 (410)	Air-smelter gas	R	2/75	Parsons	100	0.55 (1.10)	
	Monmoth Junction, N.J.	1 x 90 (100)		R	9/71	Monsanto	300	1.68 (3.38)	
Coastal Chemical Corp.	Pascagoula, Miss.	1 x 1360 (1500)	Sulfur	NA	NA	Lurgi/ Davy Powergas	NA	0.064 (0.128)	

(continued)

TABLE 5.5-3 (continued)

	Plant data				Control system data[b]				
							SO2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Dept. of Defense	Joliet, Ill.	1 x 703 (775)	Spent acid	N	3/73	Monsanto	465	3.62 (7.24)	
	Radford, Va.	1 x 453 (500)	Spent acid	N	8/72	Monsanto	500	4.13 (8.26)	
Freeport Chemical Co.	Uncle Sam, La.	1 x 1451 (1600)	Sulfur	R	/74	Chemico	NA	1.0 (1.99)	
Inspirational Consolidated Copper Co.	Inspiration, Ariz.	1 x 1706 (1880)	Air-smelter gas	N	5/77	Lurgi/ Davy Powergas	NA	NA	
Kennecott Copper Corp.	Hayden, Ariz.	1 x 725 (800)	Air-smelter gas	N	1/77	Monsanto	937	5.24 (10.48)	
Mississippi Chemical Corp.	Pascagoula, Miss.	2 x 1814 (2000)	Sulfur	N	1/72, 1/76	Lurgi/ Davy Powergas	NA	NA	
NL Industries	St. Louis, Mo.	1 x 816 (900)	Sulfur	R	/70	Lurgi/ Davy Powergas	500	3.03 (6.06)	
Standard Oil of California	El Segundo, Calif.	1 x 272 (300)	Spent acid, H_2S	N	/73	Monsanto	500	3.03 (6.06)	

(continued)

TABLE 5.5-3 (continued)

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Stouffer Chemical Co.	Dobbs Ferry, N.Y.	2 x 250 (275)	Spent acid			Lurgi/ Davy Powergas	NA	NA	
Swift Chemical Corp.	Bartow, Fla.	1 x 521 (575)	Sulfur	R		Parsons	NA	NA	
Texasgulf, Inc.	Aurora, N.C.	2 x 1383 (1525)	Sulfur	N	12/74	Monsanto	NA	0.85-0.91 (1.70-1.82)	
W.R. Grace & Co.	Bartow, Fla.	1 x 145 (160)	Sulfur	N	7/76	Monsanto	NA	0.16-1.2 (0.32-2.30)	
3M	Copley, Ohio.	1 x 146 (160)	Sulfur	R	9/76	Monsanto	NA	NA	

[a] As of December 1977.

[b] NA = Not available.

[c] kg/Mg of acid = kg SO_2/Mg of 100 percent H_2SO_4.

[d] Blank indicates no problems reported.

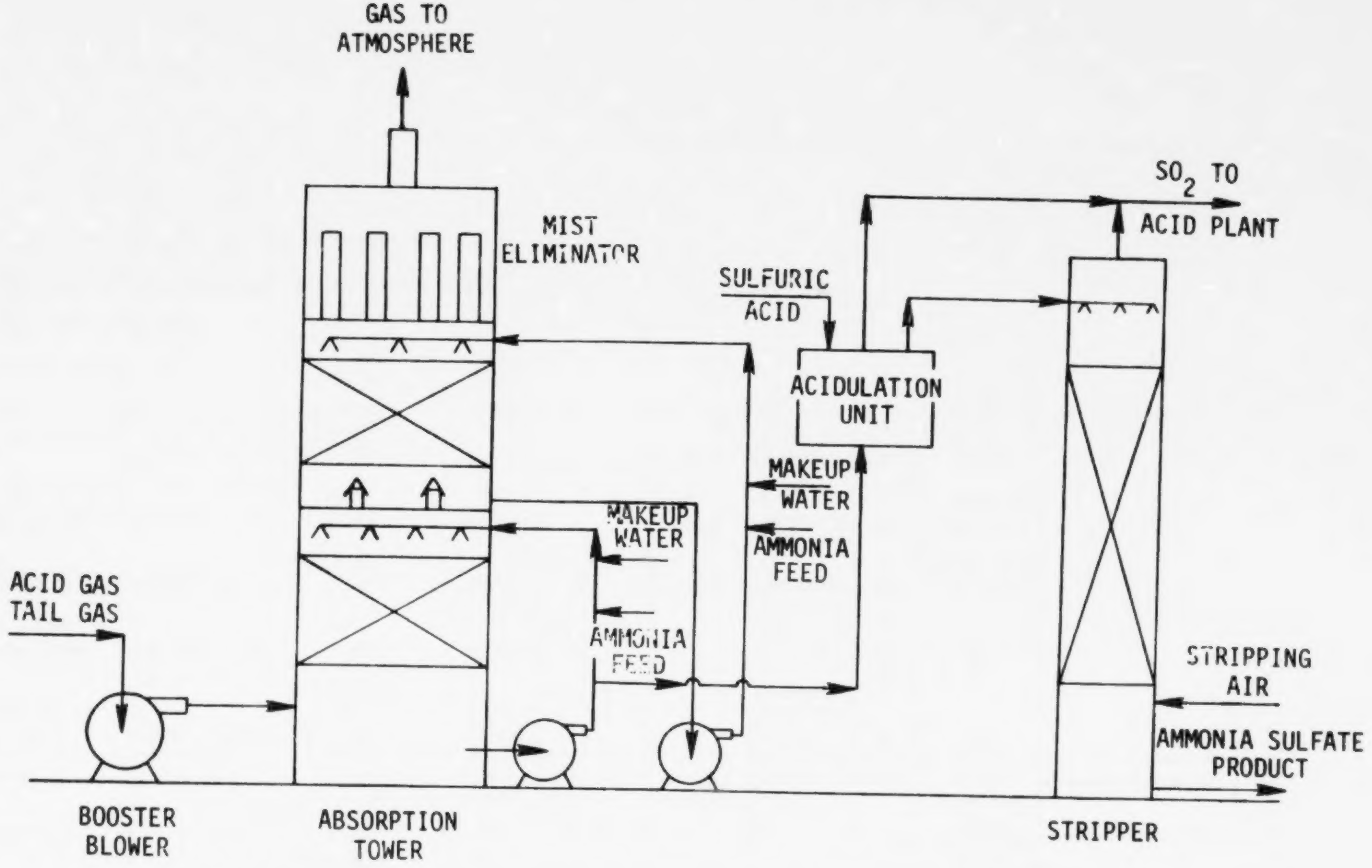

GAS TO ATMOSPHERE
MIST ELIMINATOR
SULFURIC ACID
ACIDULATION UNIT
SO_2 TO ACID PLANT
MAKEUP WATER
AMMONIA FEED
MAKEUP WATER
AMMONIA FEED
ACID GAS TAIL GAS
STRIPPING AIR
AMMONIA SULFATE PRODUCT
BOOSTER BLOWER
ABSORPTION TOWER
STRIPPER

Figure 5.5-5. Flow diagram for ammonia scrubbing of sulfuric acid plant tail gas.[14]

TABLE 5.5-4. STATUS[a] OF AMMONIA ABSORPTION SYSTEMS ON DOMESTIC SULFURIC ACID PLANTS[12]

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Allied Chemical Corp.	Newell, Pa.	1 x 453 (500)	Sulfur	R	/69	In house	300	1.76 (3.52)	Corrosion in absorber, later lined with Ceilcote
Beker Industries, Inc.	Hahnville, La.	1 x 726 (800)	Sulfur	R	12/74	Teller	150	0.93 (1.86)	Fusion of packings; corrosion of scrubber exterior; excessive pressure drop
C.F. Industries	Bartow, Fla.	1 x 771 (850)	Sulfur	R	7/75	Davy Powergas	400	2.15 (4.30)	Stack corrosion; sagging of demisters
	Bartow, Fla.	1 x 907 (1000)	Sulfur	R	6/75	Davy Powergas	600	3.64 (7.28)	
	Plant City, Fla.	NA	NA	NA	NA	Conmico	NA	NA	
Collier Carbon & Chem. Corp.	Wilmington, Calif.	1 x 408 (450)	Sulfur	R	1/74	Monsanto	500	2.87 (5.74)	Demister housing had corrosion
Conserv	Nichols, Fla.	2 x 635 (700)	Sulfur	R	10/74	Peabody	350	1.94 (3.88)	Corrosion of surrounding structure by acid mist
Farmland Industries	Bartow, Fla.	2 x 816 (900)	Sulfur	R	6/75	Davy Powergas	820	4.68 (9.36)	Blower corrosion; instrument oversizing
	Bartow, Fla.	2 x 998 (1100)	Sulfur	R	6/75		820	4.68 (9.36)	

(continued)

TABLE 5.5-4 (continued)

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems[d]
Olin Corp.	Pasedena, Tex.	1 x 635 (700)	Sulfur	N	NA	Davy Powergas	250	1.43 (2.86)	
Rohm & Haas	Deer Park, Tex.	3 x 545 (600)	Sulfur, acid sludge	R	/74	Peabody	NA	NA	
Simplot Co.	Pocatello, Idaho	1 x 1633 (1800)	Sulfur	R	/76	Monsanto	NA	NA	
W.R. Grace & Co.	Barton, Fla.	1 x 272	Sulfur	R	/66	Monsanto	NA	NA	

[a] As of December 1977.

[b] NA = Not available.

[c] kg/Mg of acid = kg SO_2/Mg of 100 percent H_2SO_4.

[d] Blank indicates no problem reported.

tion of a flue gas and of an acid plant tail gas is in the adiabatic saturation temperature, which is much lower for the tail gas. The lower moisture content of the saturated tail gas (4 percent) further enhances the mass transfer by allowing the tail gas absorber to operate at about 32°C (90°F), and fewer mass transfer stages are required for the same SO_2 removal efficiency.

Table 5.5-5 summarizes the status of sodium sulfite (Wellman-Lord) scrubbing systems on acid plants in the United States as of December 1977.[12]

Adsorption process--In adsorption systems, the tail gas is first passed through a mist eliminator and then into an adsorbent bed, which effectively removes the SO_2, SO_3, and acid mist. As the bed approaches saturation, the tail gas is passed to another bed, and the saturated bed is regenerated with a stream of hot, dry air. The effluent purge stream, rich in SO_2, is fed back into the acid plant. The adsorption/regeneration cycle operates continuously and automatically.

Even though any of the commercial adsorbents could be a suitable material, only synthetic molecular sieves or zeolites have been used in commercial applications of the adsorption process. As shown in Table 5.5-6, the process has not achieved satisfactory operations in any of the acid plants in the United States.[12]

Limestone scrubbing--Limestone scrubbing is described in detail in Section 4.2.3.2. Table 5.5-7 summarizes the status of limestone scrubbing systems on domestic sulfuric acid plants as of December 1977.

Hydrogen peroxide scrubbing[15]--One U.S. chemical company uses hydrogen peroxide (H_2O_2) scrubbing to control SO_2 emissions at two sulfuric acid plants. In this process, SO_2 in the gas stream is reacted with hydrogen peroxide to produce sulfuric acid. Dilute sulfuric acid (typically <50%) containing a small amount of H_2O_2 (<0.1%) is circulated over polypropylene packing in a scrubbing tower made of fiber-reinforced plastic. A rapid, high-yield reaction takes place in the recirculating acid medium, and the acid produced becomes part of the plant's product through blending with high-strength acid in either the drying or the absorbing towers.

TABLE 5.5-5. STATUS[a] OF WELLMAN LORD SYSTEMS ON DOMESTIC SULFURIC ACID PLANTS[12]

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems
Allied Chemical Corp.	Calumet, Ill.	1 x 907 (1000)	Sulfur	R	12/72	Davy Powergas	300	NA	Corrosion of mist eliminator; mechanical problems
Olin Corp.	Curtis Bay, Md.	1 x 635 (700)	Sulfur	R	5/73	Davy Powergas	NA	2.31 (4.62)	Evaporator tubes need periodic cleaning
	Paulsboro, N.J.	1 x 635 (700)	Sulfur	R	7/70	Davy Powergas	NA	NA	Plant operation terminated

[a] As of December 1977.

[b] NA = Not available.

[c] kg/Mg of acid = kg SO_2/Mg of 100 percent H_2SO_4.

TABLE 5.5-6. STATUS[a] OF ADSORPTION SYSTEMS ON DOMESTIC SULFURIC ACID PLANTS[12]

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems
Coulton Chemicals	Sylvania, Ohio	1 x 182 (200)	Acid sludge	R	2/73	Union Carbide	100	NA	Economically unattractive to run; company has not operated another identical system on site and is reviewing alternative control systems as replacement
Shell Oil Co.	Wood River, Ill.	1 x 182 (200)	Acid sludge	N	4/74	Anlin Co.	50	NA	Major mechanical malfunctions when Shell bought the plant from Anlin; major modifications performed to improve the process; the plant finally converted to double absorption by Monsanto

[a] As of December 1977.

[b] NA = Not available.

[c] kg/Mg of acid = kg SO_2/Mg of 100 percent H_2SO_4.

TABLE 5.5-7. STATUS[a] OF LIMESTONE SYSTEMS ON DOMESTIC SULFURIC ACID PLANTS [12]

	Plant data				Control system data[b]				
							SO_2 emissions,		
Company	Location	Capacity, No. x Mg/day (tons/day)	Feed-stock	Retrofit (R) or new (N)	Startup, mo/yr	Designer	ppmv	kg/Mg (lb/ton) acid[c]	Comments/problems
USS Agri-chemical	Bartow, Fla.	1 x 568 (625)	Sulfur	R	7/75	Peabody	200	NA	Plant operation terminated
	Ft. Mead, Fla.	1 x 1050 (1160)	Sulfur	R	7/75	Peabody	200	NA	Material for lining of scrubber has been major problem area; initial FRP lining eroded; replacement lining lasted 1 yr; scrubber needed relining in Aug. 1977

[a] As of December 1977.

[b] NA = Not available.

[c] kg/Mg of acid = kg SO_2/Mg of 100 percent H_2SO_4.

Because the reaction is

$$SO_2 + H_2O_2 \rightarrow H_2SO_4,$$

the "make" acid from the scrubber is usable as "drip" acid in lieu of dilution water. There is no byproduct and no purge stream to dispose of.

Process experience at the two plants has shown that the process is stable and easy to control. The effects of acid plant upsets are moderated by the scrubbing facility. Both plants have been in compliance with local standards covering emissions from existing sources. Although the process does not generate acid mist per se, mist entering the tail gas scrubber picks up the dilute recirculating acid; this increases the size of the droplets and the visibility of the mist. Thus, a high-efficiency mist eliminator must be used for opacity control.

No published data are available regarding the costs or energy and environmental impacts of this process. An approximate capital investment of $2.5 million, however, is reported for a 360-Mg/day (400-ton/day) plant. The electricity required for circulating scrubber reagent is about 75 kW at a circulation rate of 0.127 m^3/s (2000 gal/min). The hydrogen peroxide consumption is reported to be 0.5 kg/kg (0.5 lb/lb) of SO_2 removed.[15]

5.5.2.2 Control Costs--

Following a recent study conducted by the Tennessee Valley Authority (TVA), extensive cost data were published on retrofit emission controls applied to acid plants burning elemental sulfur.[16] The report identifies the sources of the economic data and also lists the assumptions involved. In the data on ammonia scrubbing, no credit is taken for the byproduct ammonium sulfate, and the equipment for crystallization of ammonium sulfate is not included in the capital costs. Estimates of operating costs of the Wellman-Lord process include neither credit for possible sales of byproduct sodium sulfate nor costs of disposal if the byproduct is not marketable. Because of the specialized adsorbent in the Purasiv-S process, the estimate includes a service contract for adsorbent renewal rather than costs of outright purchase of new adsorbents.

Capital costs--The data presented in Figure 5.5-6, show that on four retrofit systems the ammonia scrubbing process is the least expensive, the

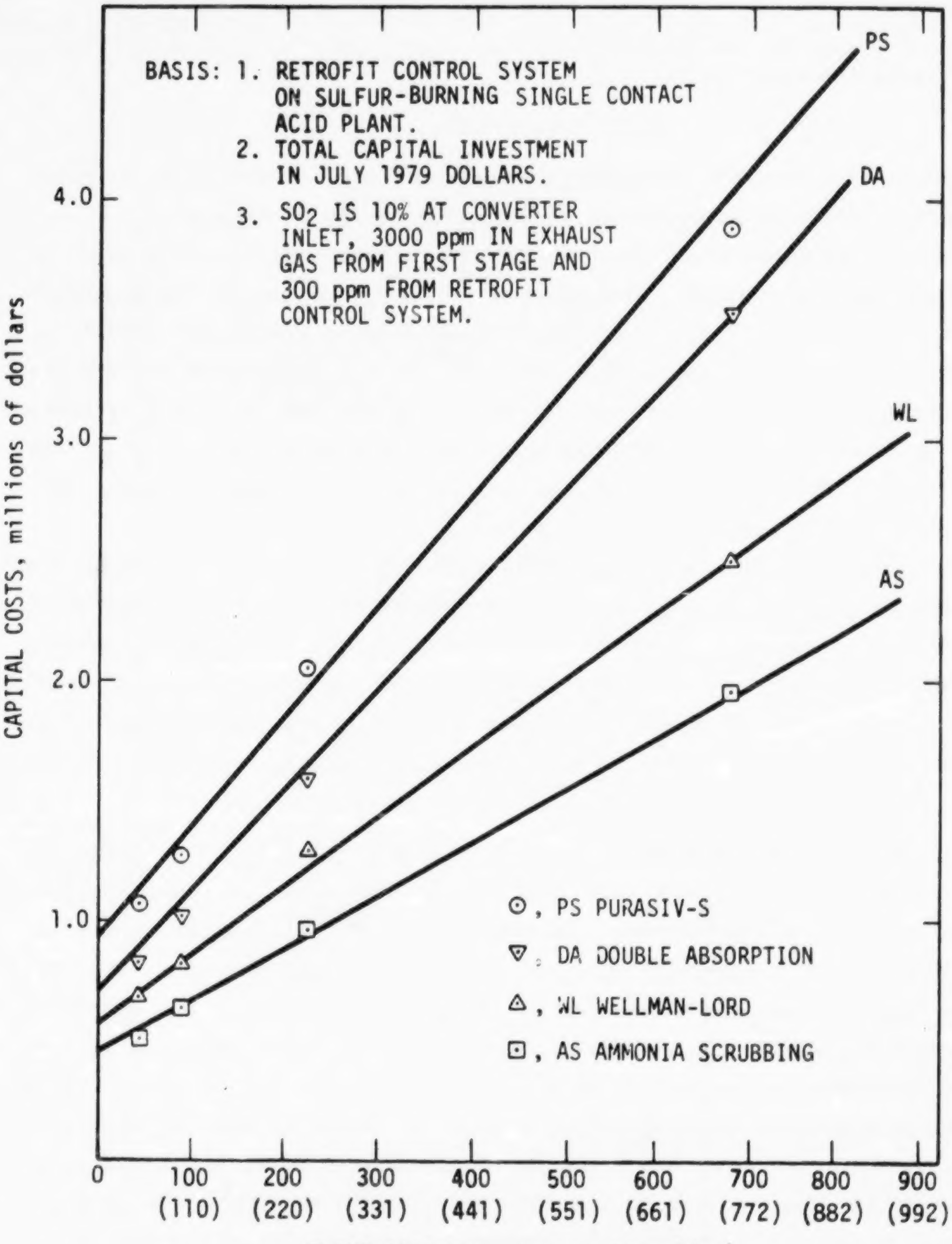


Figure 5.5-6. Capital costs of SO_2 control systems for domestic sulfuric acid plants.[16]

Wellman-Lord system is more expensive, and the two most capital-intensive systems are the double adsorption and Purasiv-S processes. These costs are for a sulfur-burning contact acid plant with SO_2 concentration at the converter inlet of 10 percent. For cold gas plants, which have lower SO_2 concentrations and higher gas volumes, the costs will be much higher.

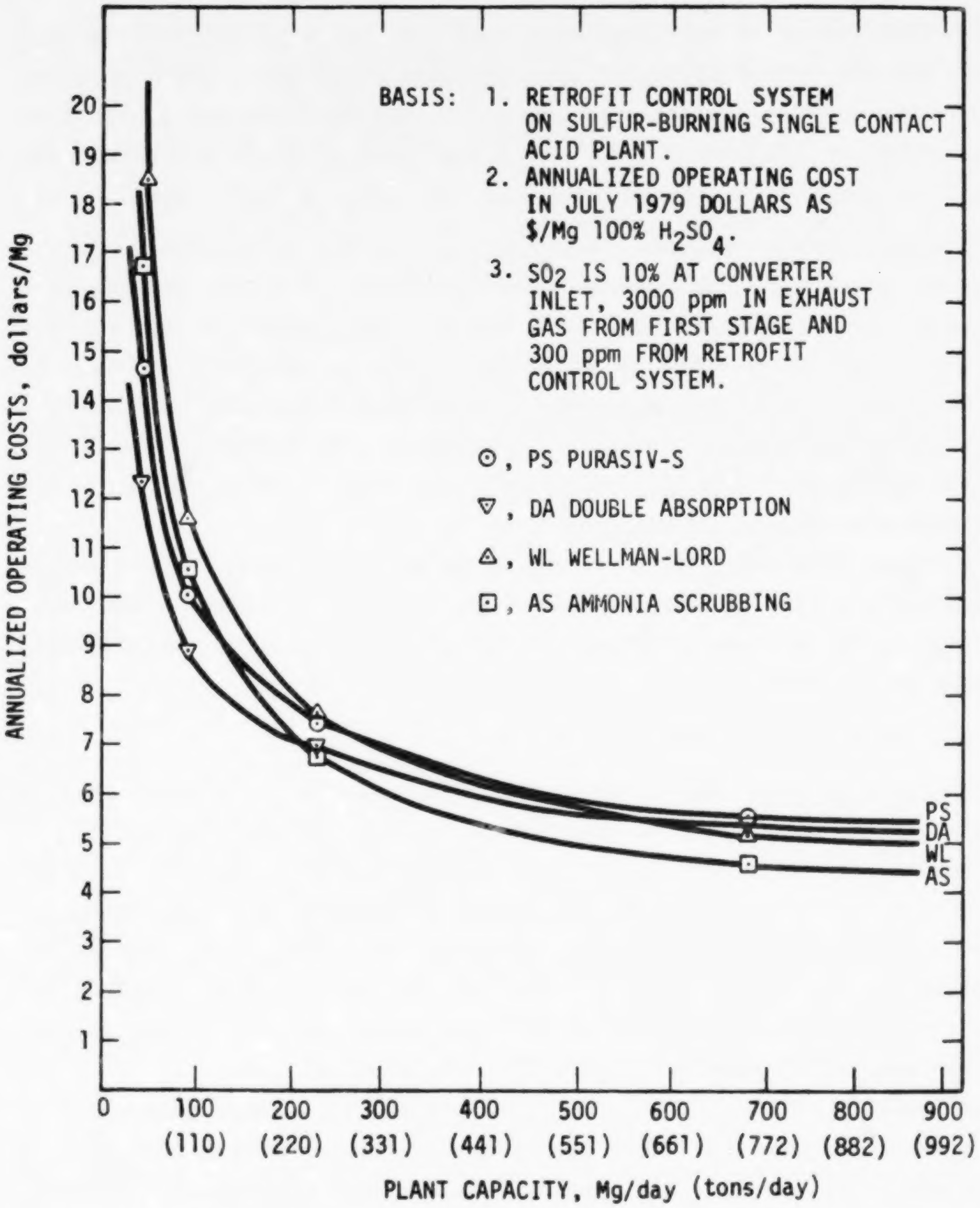
Operating costs--The data in Figure 5.5-7 show considerable variation in overall operating costs, depending on plant size. The data indicate that the double absorption and Purasiv-S systems are cheaper to operate for plants with capacities of 45 to 90 Mg/day (50 to 100 tons/day). For plants producing 227 Mg/day (250 tons/day), the double absorption and ammonia scrubbing are the least expensive to operate; and for plants producing 680 to 1360 Mg/day (750 and 1500 tons/day), the lowest operating costs are associated with ammonia scrubbing.

Application of the ammonia scrubbing system would mainly depend on the marketability of the generated ammonium sulfate as fertilizer. The costs will also depend on such site-specific factors as location and availability of space for retrofit.

5.5.2.3 Energy and Environmental Impacts--

Double absorption--Double absorption can reduce SO_2 emissions below 300 ppm and SO_3 and acid mist emissions below 0.05 g/Nm^3 (0.022 gr/ft^3).[12] It produces no solid or liquid waste stream and thus has no secondary pollution effects. In addition, the sulfur consumption is low; in comparison with a single absorption plant operating at 97 percent conversion and producing 907 Mg/day (1000 ton/day) of 100 percent acid for 350 days/year, a double absorption plant at 99.7 conversion and the same production rate consumes nearly 2900 Mg (3200 tons) less sulfur per year.

A double absorption plant, however, consumes more energy and produces less bonus steam than its single absorption counterpart because the gas from the primary absorber must be reheated to conversion temperature. Further, extra power is needed for the blower, more cooling water circulation is required, and the acid recirculation pumps for the added absorber consume extra power. Together, these typically add the equivalent of 4 MW to the power demand of a 907-Mg/day (1000-ton/day) acid plant.[17]



BASIS:
1. RETROFIT CONTROL SYSTEM ON SULFUR-BURNING SINGLE CONTACT ACID PLANT.
2. ANNUALIZED OPERATING COST IN JULY 1979 DOLLARS AS \$/Mg 100% H_2SO_4.
3. SO_2 IS 10% AT CONVERTER INLET, 3000 ppm IN EXHAUST GAS FROM FIRST STAGE AND 300 ppm FROM RETROFIT CONTROL SYSTEM.

Figure 5.5-7. Operating costs of SO_2 control systems for domestic sulfuric acid plants.[16]

Adsorption process--The Purasiv-S system is completely equivalent to the double absorption system in environmental impact. It could, in fact, reduce the SO_2 emissions below 50 ppm; however, as shown in Table 5.5-6, this process has not proved to be commercially successful.

The energy penalty, primarily due to the pressure drop in adsorber/regenerator and the heating of ambient air used for regeneration of adsorbent, would be equivalent to about 1 MW for a 907-Mg/day (1000-ton/day) plant.[18]

Ammonia scrubbing--Ammonia scrubbing can achieve SO_3 and acid mist removal comparable to that by the double absorption process. It often operates at 90 percent SO_2 removal efficiency. The process generates ammonium sulfate (liquor or crystals) as a byproduct and may cause formation of a blue haze from emission of very fine particles of ammonium sulfate and sulfite.

Primary energy consumption is by the blower to overcome the pressure drops in the absorber and the stripper, and by the recirculation pumps. Based on data for combustion sources, the energy penalty for a 907-Mg/day (1000-ton/day) plant is estimated to be equivalent to 0.6 MW.

Sodium sulfite scrubbing--The environmental impact of sodium sulfate scrubbing is identical to that of ammonia scrubbing except that it does not produce blue haze and the byproduct is sodium sulfate instead of ammonium sulfate.

The energy penalty would be greater than for the ammonia scrubbing process because the evaporators in the regeneration subsystem consume steam. Again, based on data for combustion sources, the energy penalty for a 907-Mg/day (1000-ton/day) plant will be about 1.1 MW.

Limestone scrubbing--Although limestone scrubbing provides adequate removal of the pollutants (SO_2, SO_3, and acid mist), it also generates a waste product, calcium sulfite/sulfate sludge, that needs proper handling and disposal. The sludge could be thickened, dewatered, stabilized, and landfilled; however, operators of limestone FGD systems on combustion sources currently tend to discharge unstabilized sludge to settling ponds.

The primary pieces of energy-consuming equipment are the booster blower, recirculation pumps, ball mill (if any), thickener, filter, and conveyors and pumps. The overall energy penalty for a 907-Mg/day (1000-ton/day) plant is estimated to be 0.8 MW.

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5.6 PULP MILLS

Pulp and paper manufacturing, one of the 10 largest industries in the United States, is conducted in two phases: pulping of wood, and production of paper and related products from the pulp. In the pulping process, wood is reduced to fiber, sometimes bleached, and dried. Most pulp mills use a chemical cooking liquor to dissolve lignins and free the wood fibers, then recover the chemicals by a combustion process. The pulp manufacturing process generates gaseous and particulate emissions in quantities that depend on the type of pulping operation, the type of recovery process, and the effectiveness of control equipment.

5.6.1 Process Descriptions and Emission Sources

Three major pulping and recovery processes account for nearly 80 percent of the pulp produced in this country: sulfate (kraft), sulfite, and neutral sulfite semichemical (NSSC). The other 20 percent is produced by specialized processes.

The sulfate or kraft process has created the greatest air pollution problem, mainly because of the large quantity of visible particulates and highly odorous reduced sulfur compounds. Acid-based sulfite and neutral sulfite pulping mills are important in this study because, more than other types of mills, they emit SO_2. Many of these mills use highly efficient SO_2 absorption systems as part of the chemical recovery system.

5.6.1.1 Sulfate Process--

As with most modern pulping processes, kraft or sulfate pulping (Figure 5.6-1) begins in a digester, where wood chips from debarked logs are cooked with a chemical solution. In the kraft process, the cooking solution, known as white liquor, is sodium hydroxide (caustic soda) and sodium sulfide. The caustic soda in the cooking liquor permits the pulping of nearly all wood species. The liquor and wood chips are carefully cooked under controlled conditions of temperature and pressure. During digestion the liquor dissolves the lignin in the wood and thus frees the cellulose fibers. When the cooking is completed, the residual pressure within the digester is used to force the contents to a blow tank. The sudden decrease in pressure and the

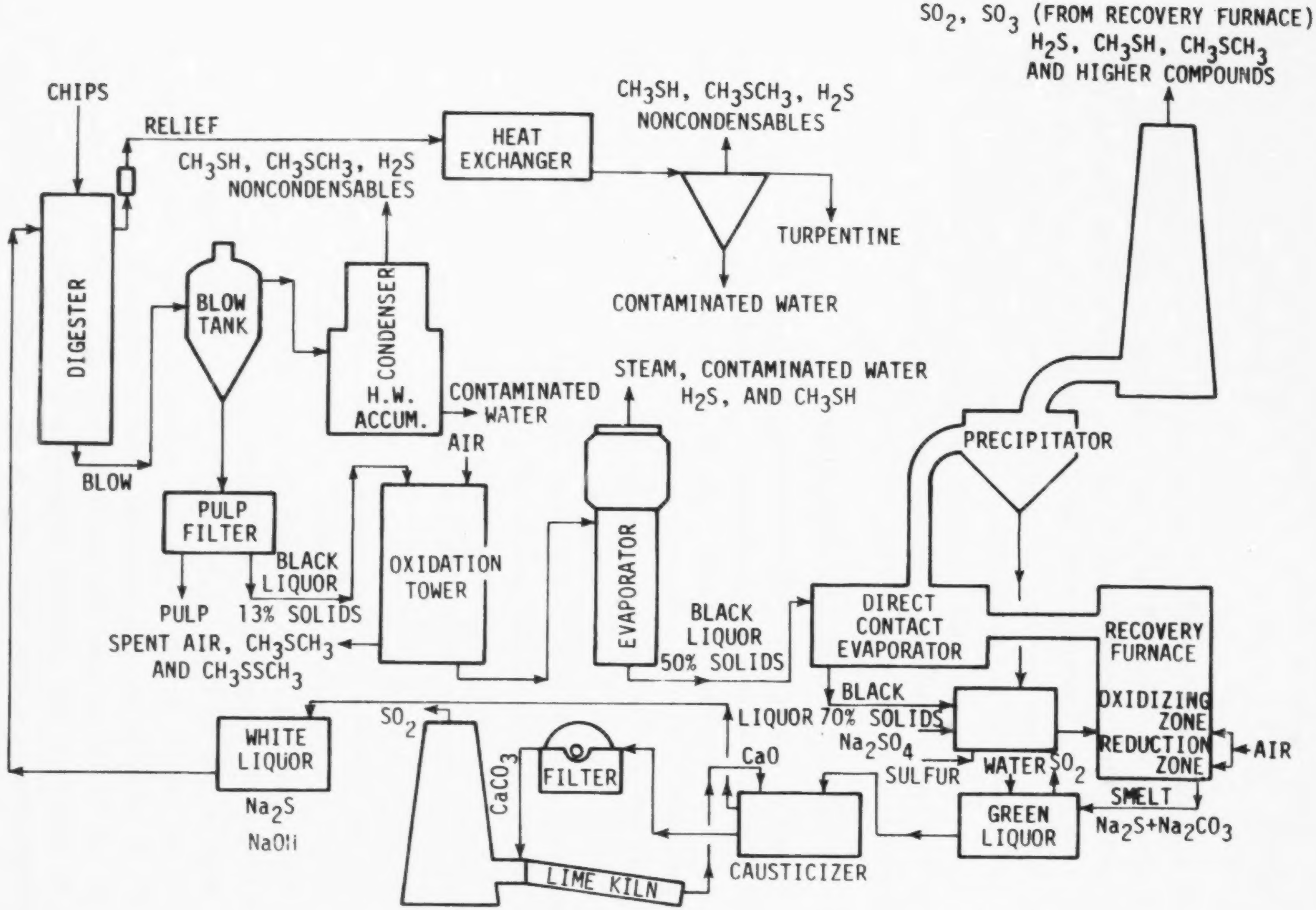
SO_2, SO_3 (FROM RECOVERY FURNACE)
H_2S, CH_3SH, CH_3SCH_3
AND HIGHER COMPOUNDS
CHIPS
RELIEF
HEAT EXCHANGER
CH_3SH, CH_3SCH_3, H_2S
NONCONDENSABLES
CH_3SH, CH_3SCH_3, H_2S
NONCONDENSABLES
TURPENTINE
CONTAMINATED WATER
DIGESTER
BLOW TANK
CONDENSER
H.W. ACCUM.
CONTAMINATED WATER
STEAM, CONTAMINATED WATER
H_2S, AND CH_3SH
PRECIPITATOR
AIR
BLOW
PULP FILTER
BLACK LIQUOR
OXIDATION TOWER
EVAPORATOR
PULP
13% SOLIDS
SPENT AIR, CH_3SCH_3
AND CH_3SSCH_3
BLACK LIQUOR
50% SOLIDS
DIRECT CONTACT EVAPORATOR
RECOVERY FURNACE
OXIDIZING ZONE
REDUCTION ZONE
AIR
BLACK LIQUOR 70% SOLIDS
Na_2SO_4
SULFUR
WATER
SO_2
WHITE LIQUOR
Na_2S
NaOH
SO_2
$CaCO_3$
FILTER
CaO
GREEN LIQUOR
SMELT
$Na_2S+Na_2CO_3$
LIME KILN
CAUSTICIZER

Figure 5.6-1. Typical kraft sulfate pulping and recovery process showing potential emission sources.

impact against the tank walls cause the soft wood chips to explode and become a fiber pulp. Gases and steam from the blow tank are vented to a condenser. The noncondensable gases, which are the sources of odors, are either confined and treated or released to the atmosphere.

The pulp, containing spent liquor (called black liquor), is diluted in the blow tank and then is pumped to washers. The pulp is washed countercurrently to remove black liquor and waste wood products. The pulp may be bleached and sent to subsequent operations for formation of paper products or dried and sold as market pulp.

A typical kraft waste liquor recovery process begins with multiple-effect evaporators, to which black liquor containing about 15 percent solids is pumped from the pulp washers. The liquor is further concentrated in direct-contact or forced-circulation concentrators to a concentration of 60 to 70 percent solids. Weak liquor from the pulp washers or strong black liquor from the multiple-effect evaporators is pumped through an oxidation tower to facilitate odor control and chemical recovery. Oxidation converts sodium sulfide to innocuous salts to prevent the release of hydrogen sulfide.[1]

The concentrated black liquor then is sprayed into a recovery furnace, where the organic content supports combustion. The inorganic compounds, consisting of the cooking chemicals, fall to the bottom of the furnace where they form a molten smelt that drains into a smelt-dissolving tank. The dissolved smelt, containing mainly sodium sulfide, sodium sulfate, and sodium carbonate, is called green liquor.

The green liquor is clarified, then mixed with slaked lime in a causticizer to give products of sodium hydroxide, sodium sulfide, and calcium carbonate. The calcium carbonate is removed in a clarifier; the resultant clarified (white) liquor is recycled as cooking solution. The calcium carbonate is pumped to a thickener, then discharged into a rotary kiln to produce lime, which is sent back to the slaker.

Various reactions among the kraft mill cooking chemicals generate characteristic gaseous emissions, including malodorous reduced sulfur compounds. Such compounds are methyl mercaptan (CH_3SH), hydrogen sulfide (H_2S), dimethyl sulfide (CH_3SCH_3), and dimethyl disulfide (CH_3SSCH_3). Kraft mills also generate oxides of sulfur, but to a much lesser degree. The major source of SO_2 emissions is the recovery furnace in which the sulfur-containing black liquor undergoes combustion. The furnace can emit some SO_3 under certain conditions. Table 5.6-1 shows typical SO_2 and SO_3 emissions from kraft pulp mill combustion sources.

Concentrations of SO_2 from the recovery furnace depend on the following: 1) sulfidity of the cooking liquor, 2) manner in which liquor is sprayed into the furnace, 3) ratio of primary to secondary combustion air, and possibly 4) liquor firing temperature.[2] Lesser quantities of SO_2 can be released from the lime kiln and smelt dissolving tank.

The major potential sources of particulate emissions are the same sources that generate SO_2 (i.e., the recovery furnace, smelt dissolving tank, and lime kiln).

For kraft process units, the process information on various pieces of equipment is given in Table 5.6-2.

5.6.1.2 Sulfite Process--

Sulfite pulping is similar to kraft pulping except that a sulfurous acid base solution is used to dissolve the lignin in the wood chips rather than a caustic solution. A bisulfite of sodium, calcium, ammonia, or magnesium is used to buffer the cooking solution.

After the wood chips have been cooked in a digester, the pressure in the digester is reduced and the contents are charged to the blow tank, where the chips are defibered. The pulp is screened for knots and foreign substances such as grit, then separated from the spent liquor in a series of washers. The pulp is sent on for bleaching and finally the papermaking process.

In the past, much of the spent sulfite cooking liquor was discharged to sewers, but greater emphasis is now placed on burning the liquor, which supports combustion when concentrated to approximately 55 percent solids content, to reduce liquid effluent, recover chemicals, and generate steam.

In calcium-based systems (only relatively few are now operating), chemical recovery is not economically practical. Some mills thicken the liquor in evaporators and sell it for use in various products such as animal

TABLE 5.6-1. TYPICAL EMISSION CONCENTRATIONS AND RATES FOR SO_x FROM KRAFT PULP MILL COMBUSTION SOURCES[3]

Emission source	Concentration, ppm by vol.		Emission rate, kg/Mg	
	SO_2	SO_3	SO_2	SO_3
Recovery furnace:				
No auxiliary fuel	0-1,200	0-100	0-40	0-4
Auxiliary fuel added	0-1,500	0-150	0-50	0-6
Lime kiln exhaust	0-200		0-1.4	
Smelt dissolving tank	0-100		0-0.2	

TABLE 5.6-2. KRAFT PROCESS EQUIPMENT DATA[4]

Variable	Recovery furnace	Lime kiln	Digester relief and blow tank	Dissolving tank
Gas flow rate, Nm^3/Mg (scf/ton) [air dried pulp basis]	8490 (272,000)	1190 (38,100)	4.23 (137) [continuous digester] 8.55 (274) [batch digester]	1130 (36,100)
Gas temperature				
At precipitator				
Average, °C (°F)	163 (325)			
Range, °C (°F)	163 to 191 (325 to 375)			
After scrubber (if used)				
Range, °C (°F)	74 to 93 (165 to 200)			71 (160)
At exit, °C (°F)		82 (180)	49 (120)	
Uncontrolled, °C (°F)				93 (200)
Gas velocity				
Range, m/s (ft/s)	4 to 11 (13 to 36)			
Typical, m/s (ft/s)	9.1 (30)	6.1 (20)[a]	6.1 (20)[a]	6.1 (20)[a]
Stack height				
Range, m (ft)	38 to 122 (125 to 400)			
Typical, m (ft)	76 (250)	9.1 (30)[a]	9.1 (30)[a]	9.1 (30)[a]

[a] Estimated, no data available.

feed and dispersants. For environmental reasons, one mill did install a recovery system in mid-1973 as a standby for use when the thickened liquor cannot be sold.[5]

When recovery is practical in magnesium-, sodium-, and ammonium-based systems, the spent liquor is pumped through multiple-effect evaporators and then is sprayed into a recovery furnace, similar to that in the kraft process. When the magnesium-based liquor is burned, magnesium oxide (MgO) particles and SO_2 are liberated and exit with the flue gas. The MgO is collected in cyclones and later slaked to form a magnesium hydroxide [$Mg(OH)_2$] slurry. The hot gas stream containing SO_2 leaving the cyclones is cooled, and the SO_2 is absorbed by the $Mg(OH)_2$ in absorption towers to produce the usable pulping acid. This system is described later in more detail.

Recovery of chemicals to regenerate pulping acid in the sodium-based system is somewhat more involved than the MgO system. Usually the sodium-based liquor is burned in a reducing atmosphere. The flue gas contains SO_2 and some sodium sulfate particles, which are collected in electrostatic precipitators and returned to the furnace. Most of the inorganic dry solids fall to the bottom of the furnace and form a smelt consisting of sodium sulfide and sodium carbonate. When the market is good, some sodium-based mills can sell the smelt to kraft mills for use in their process as "green liquor." The SO_2 from the furnace is cooled and passed through an absorber utilizing a sodium carbonate scrubbing solution. The resultant solution, sodium sulfite/bisulfite, is returned as pulping acid. Sodium-based mills that totally recover their furnace products utilize one of several modern recovery processes (e.g., Stora, SCA-Billerud, Tampella). The Stora process, which is commonly used, is described in the following paragraph.

The smelt from the recovery furnace is dissolved in water and clarified. The resulting "green liquor" is carbonated with pure carbon dioxide. The sodium sulfide is converted to H_2S, which is stripped from the liquor by carbon dioxide as the carrier gas. The H_2S reacts in a Claus reactor with SO_2 to form elemental sulfur. The carbon dioxide is recirculated to the process. In this way the green liquor is converted to sodium bicarbonate ($NaHCO_3$), which is then reacted with sodium bisulfite to produce sodium sulfite.[6] Part of the sulfite solution absorbs SO_2 in an absorption tower and is returned as sodium bisulfite. The sodium sulfite is returned to the pulping process as pulping acid.

Ammonium-based mills can practice only partial recovery, by burning the spent liquor, cooling the flue gas, and absorbing the SO_2 in the flue gas with an ammonium hydroxide slurry to produce ammonium sulfite/bisulfite pulping acid. The ammonium base is broken down to nitrogen, nitrogen oxides, and water vapor during combustion and thus cannot be recovered.

Unlike the kraft pulping process, in which the cooking solution contains sulfide/sulfate chemicals, the sulfite pulping cooking liquor contains a sulfurous-acid base and sulfite/ bisulfite compounds. When heated, these latter compounds give off considerable quantities of SO_2. Because sulfides are not present, no organic reduced sulfur compounds are produced in the sulfite process. Hydrogen sulfide emissions may occur if alkaline sulfite liquor is burned in recovery furnaces under reducing conditions.[7]

The main sources of SO_2 emissions at sulfite mills are the digester blow tanks, multiple-effect evaporators, and the chemical recovery system (if recovery is practiced). The makeup acid preparation plant and the pulp washers are minor sources of SO_2. Table 5.6-3 shows a range of typical emission factors from controlled and uncontrolled sources of SO_2.

For sulfite process units, process information on various pieces of equipment is given in Table 5.6-4.

5.6.1.3 Neutral Sulfite Semichemical Process--

The NSSC process differs from the kraft and sulfite pulping processes in two major aspects. The cooking liquor is a neutral solution of sodium sulfite and sodium bicarbonate or sodium carbonate, rather than being acidic or basic. The sulfite ion reacts with the lignin in the wood, and the sodium bicarbonate acts as a buffer to maintain a neutral solution.[8] More importantly, only a portion of the lignin is dissolved in the digester during cooking. The partially cooked wood chips then are subjected to mechanical attrition to produce the pulp. This chemical/mechanical method produces pulp yields of up to 80 percent, versus 42 to 58 percent yields typical of complete chemical pulping processes.[9]

TABLE 5.6-3. TYPICAL SO_2 EMISSION FACTORS FOR SULFITE PULP MILL SOURCES[10]

Emission source	Emissions, kg/Mg (lb/ton)[a]	
	Uncontrolled	Controlled[b]
Blow pit:		
Hot blow	30-75 (60-150)	1-2.5 (1-5)
Cold blow	2-10 (4-20)	0.05-0.3 (0.1-0.6)
Evaporators	1-30 (2-60)	0.025-1 (0.05-2)
Recovery process	80-250 (160-500)	6-20 (12-40)
Washers	0.5-1 (1-2)	
Acid preparation	0.5-1 (1-2)	

[a] Per mass, Mg (ton), of air dried pulp.

[b] Alkaline scrubbing of gases.

TABLE 5.6-4. SULFITE PROCESS EQUIPMENT DATA[11]

Variable	Recovery furnace	Digester relief and dump tank
Gas flow rate, Nm^3/Mg (scf/ton) [air dried pulp basis]	9270 to 10,590 (297,000 to 339,200)	12.9 (414)
Gas temperature		
Average, °C (°F)	74 (165)	82 (180)
Range, °C (°F)		27 to 121 (80 to 250)
Gas velocity[a], m/s (ft/s)	6.1 (20)	6.1 (20)
Stack height[a], m (ft)	61 (200)	9.1 (30)

[a] Estimated, no data available.

The fate of spent liquor from the pulp washers depends on arrangements at the specific pulp mills. Some mills recover the cooking chemicals in a manner similar to that used at sulfite mills, i.e., by concentrating the spent liquor and then burning it in a recovery boiler. Mills without NSSC recovery systems treat and discharge the spent liquor; if a kraft operation is nearby, the NSSC spent liquor can be mixed with that from the kraft process and burned in the kraft recovery furnace. The recovered chemicals are used entirely in the kraft system.

The digester and blow tank emit SO_2 during the digester relief and blow. In batch-type digesters, however, the SO_2 pressures during neutral sulfite cooking are considerably lower than those exerted in acid bisulfite cooking; thus SO_2 emissions from NSSC sources are lower than those from sulfurous-acid-based (sulfite) operations. The evaporators are another source of SO_2, usually less than 1 kg SO_2 per Mg of pulp (2 lb SO_2/ton of pulp).[12] At NSSC mills with a recovery furnace (sometimes a boiler, reactor, or waste liquor incinerator), this unit is the main potential source of SO_2 emissions.

For NSSC process units, process information on various pieces of equipment is given in Table 5.6-5.

5.6.2 Control Techniques

Use of the various SO_2 control techniques described here depends on site-specific factors such as the type of pulping operation, quantities of SO_2 emitted, the applicable environmental regulations (particularly concerning air and water), problems associated with retrofitting control equipment, and the economics of obtaining and operating the controls. Often the end products of the SO_x controls are chemicals that can be reused in the pulping operation and serve as a credit to offset operating costs.

5.6.2.1 Description--

Sulfate process--Although it is the malodorous sulfur compounds and not SO_2 that pose the greatest air pollution problem at sulfate mills, there is generally always some release of SO_2 from such mills, particularly from the recovery boilers. Control devices are not used specifically for SO_2 control at sulfate mills, but reduction of the pollutant can take place in certain

TABLE 5.6-5. NSSC PROCESS EQUIPMENT DATA[13]

Variable	Blow tank	Absorption tower	Recovery furnace	Fluidized bed reactor
Gas flow rate, Nm^3/Mg (scf/ton) [air dried pulp basis]	540 to 860 (17,350 to 27,600)	110 (3400)	700 (22,500)	3800 (121,700)
Gas temperature				
At exit				
Range, °C (°F)	93 to 100 (200 to 212)			
Typical, °C (°F)	100 (212)	38 (100)		
After precipitator, °C (°F)			163 (325)	
After venturi, °C (°F)				82 (180)
Gas velocity[a], m/s (ft/s)	6.1 (20)	6.1 (20)	6.1 (20)	6.1 (20)
Stack height[a], m (ft)	9.1 (30)	9.1 (30)	61 (200)	9.1 (30)

[a] Estimated, no data available.

process equipment. For example, the direct contact evaporator used at most kraft mills to concentrate black liquor also acts to absorb about 75 percent of the SO_2 emitted from the recovery boiler and nearly all of the SO_3 (concentrations shown in Table 5.6-1).[14]

Lime kilns and fluidized bed calciners, although sources of SO_2 at kraft mills, are generally low emitters (given as about 34 ppm SO_2 in one report)[15] because once SO_2 is formed, most of it reacts with lime and forms calcium sulfite and calcium sulfate. In kilns equipped with wet scrubbers for control of particulate matter, this reaction is particularly effective. In a limited series of tests of a fluidized bed calciner, it was not possible to measure the presence of SO_2 in the exhaust gases.[16]

Tests of lime kilns in lime manufacturing plants showed that SO_2 removal efficiency with dry control devices ranged from 82 to 93 percent.[17] Normally dry control devices do not remove SO_2 but in this case the intimate contact between lime particulate from the kiln and the SO_2 occurs in the kiln, and also in the duct and control device. These kilns ranged in size from about 18 to 155 Mg/h (20 to 171 tons/h). Tests on three kilns using high-sulfur coal with wet scrubbers showed removal efficiencies of 98 to 99.5 percent.[17] Outlet SO_2 concentrations for all cases except one ranged from 5 to 45 ppm. One particularly large kiln (155 Mg/h or 171 tons/h) firing high-sulfur coal had an outlet concentration of 199 ppm.[17]

Sulfite process--Emissions from the blow tank/pit and evaporator containing SO_2 need not be vented to the atmosphere, but can be directed to acid towers. The acid towers are used to produce makeup cooking acid, usually by absorbing SO_2 (produced from sulfur burners) with a solution of the hydroxide of the base used for making pulp (e.g., magnesium hydroxide). Proper introduction of SO_2-laden gas streams from digester blows and evaporator vents to the acid towers can adequately control SO_2 emissions from these two sources. Information from a 127-Mg/day (140-ton/day) calcium-based sulfite mill shows that emissions from their acid tower vent before and after tie-in of the digester blow stack emissions and evaporator vent emissions remained approximately the same at 0.54 Mg (0.6 ton) of SO_2 per day.[18] Similar findings are reported at another calcium-based sulfite mill in which digester off-gases and the SO_2 stream from a spent liquor flash tank are tied into the mill's acid tower.[19]

Chemical recovery systems are operated at all types of sulfite pulping mills, whether the process is magnesium, calcium, ammonia, or sodium based. Many sulfite mills installed the recovery systems because environmental regulations prohibit discharge of the spent liquor to water bodies (e.g., streams, rivers) and the mills cannot market the liquor. Recovery of the cooking chemicals is important today, especially at magnesium-based sulfite mills, because of the cost of makeup chemicals. Installation of a chemical recovery system reduces water pollution problems but causes generation of SO_2 from the recovery boiler, furnace, or incinerator. The purpose of the recovery boiler, however, in addition to burning the organic portion of the thickened liquor to generate steam for mill use, is to liberate the SO_2 (as a gas) and inorganic solids (as particulates or as smelt) so that they can be collected and reused in the pulping operation.

In a typical SO_2 control/recovery system at a magnesium-based operation, SO_2 and magnesium oxide from the recovery furnace (Figure 5.6-2) are passed through cyclones to remove most of the magnesium oxide, which is discharged to a slurrying tank. The hot gas stream containing SO_2 exits the cyclones and is cooled in a scrubber and/or cooling tower. The cooled SO_2 stream then is sent through absorption towers (often a series of three), in which the SO_2 is absorbed by a magnesium hydroxide slurry pumped from the slurry tank. The absorption product is a slurry containing magnesium bisulfite and sulfurous acid; the slurry is returned to the pulping operation as cooking acid for the digesters.

Although the recovery boiler generates the SO_2, it is actually the absorption towers (which are not 100 percent efficient) that emit the SO_2 from the chemical recovery system; i.e., the absorption towers are an integral part of the recovery system and are not a control system per se. Nonetheless, because the absorbers are reported to operate at high SO_2 removal efficiencies (95 percent plus at many mills) and with high operability, they are considered here as an important SO_2 control technique.[20]

It is important for chemical recovery and for meeting SO_2 regulations that the absorption systems do operate reliably and efficiently. If further SO_2 control is required, another absorption tower(s) with auxiliary equipment such as fans could be installed to receive off-gas from the recovery

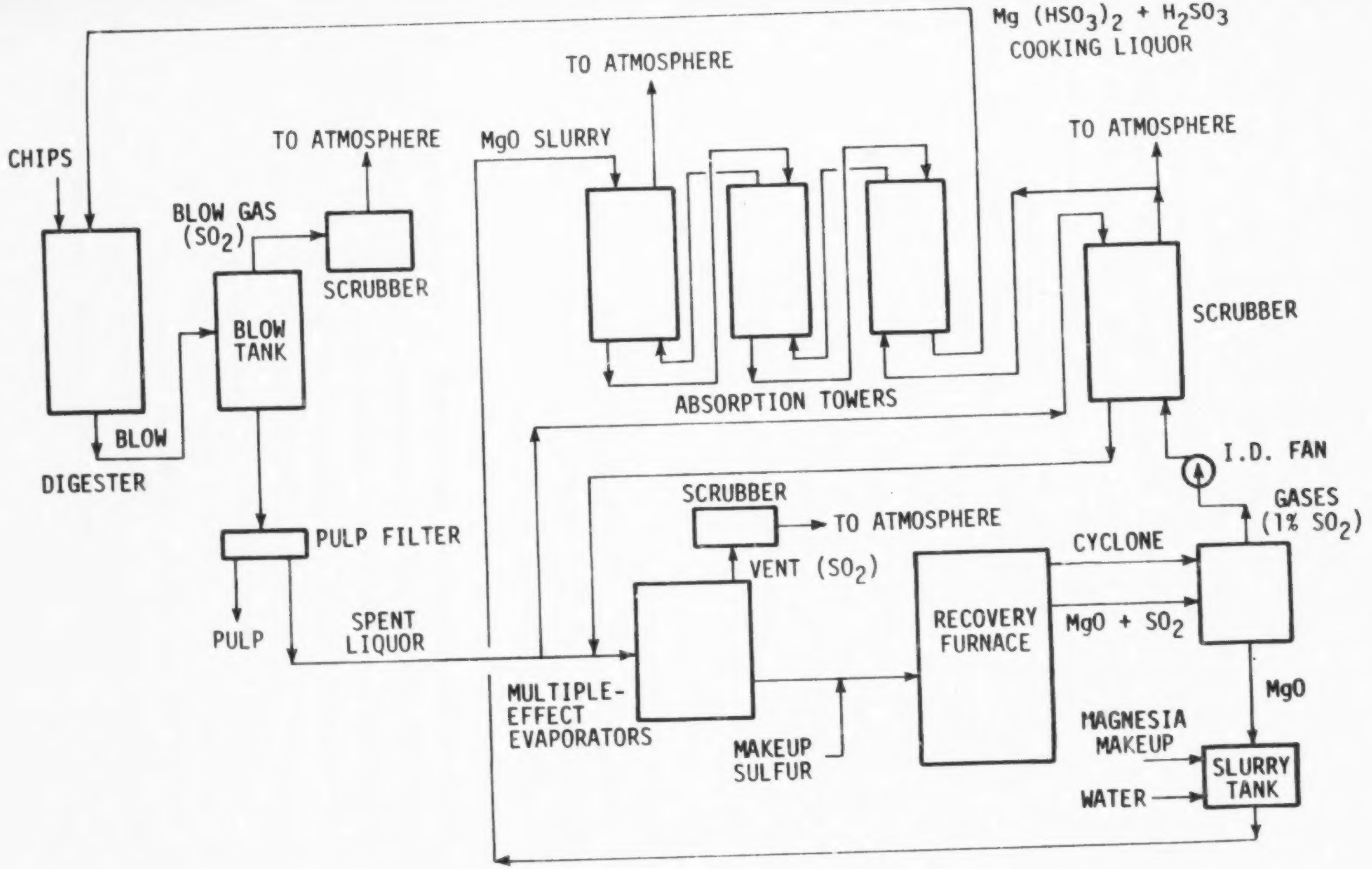
Mg $(HSO_3)_2$ + H_2SO_3
COOKING LIQUOR
TO ATMOSPHERE
TO ATMOSPHERE
MgO SLURRY
TO ATMOSPHERE
CHIPS
BLOW GAS (SO_2)
SCRUBBER
BLOW TANK
SCRUBBER
ABSORPTION TOWERS
BLOW
DIGESTER
I.D. FAN
SCRUBBER
TO ATMOSPHERE
GASES (1% SO_2)
PULP FILTER
CYCLONE
VENT (SO_2)
SPENT LIQUOR
PULP
RECOVERY FURNACE
MgO + SO_2
MULTIPLE-EFFECT EVAPORATORS
MgO
MAGNESIA MAKEUP
MAKEUP SULFUR
SLURRY TANK
WATER

Figure 5.6-2. Typical magnesium-based chemical pulping recovery process showing potential emission sources.

absorption tower. Operators of one magnesium-based sulfite process installed an ammonia absorption system to reduce SO_2 emissions from the magnesium hydroxide absorption towers. It was reported that the ammonia system reduced the SO_2 concentration from approximately 2500 ppm to 390 ppm for a control efficiency of 84.5 percent.[21]

Neutral sulfite semichemical process--At NSSC mills that thicken their spent liquor and burn it in recovery furnaces, the SO_2 generated is generally removed or controlled in absorption towers with a sodium carbonate solution as the absorbent. Product from the tower is mainly sodium bicarbonate, which is used in the digester cooking liquor. Smelt from the recovery furnace consists of sodium carbonate and sodium sulfide. The sulfide is not usable in the NSSC cooking liquor. In the Mead process, the clarified smelt solution is treated with a gas containing carbon dioxide, which converts the sodium sulfide to sodium bicarbonate while expelling hydrogen sulfide; the hydrogen sulfide is converted by pyrolysis in the presence of excess air to SO_2, which together with the SO_2-containing flue gas from the liquor recovery process is brought into contact with carbonated liquor in an absorption (SO_2 control) system to produce fresh cooking liquor containing sodium sulfite and sodium bicarbonate.[22]

The SO_2 from other NSSC process sources (e.g., evaporators) can be routed to the chemical recovery absorption towers or to cooking liquor (acid) makeup towers.

5.6.2.2 Control Cost--

Data on costs of the techniques for controlling SO_2 at pulp mills often are not available, and it is difficult to formulate estimates that represent a typical installation. Mill operators control SO_2 in various ways, even at mills of similar size with similar process steps. One mill may purchase special equipment for SO_2 reduction, while another mill converts unused onsite equipment into usable SO_2 control components. Also, although data on costs of chemical recovery at a mill might be available, they seldom show the costs of specific SO_2 absorption equipment.

The following cost information from trade journals pertains to specific mills. All costs are updated to July 1979 through the use of Chemical Engineering cost indices.

In January 1975 an emission control system to recover SO_x, remove particulates, and recover heat from a recovery boiler was retrofitted to ITT Raynoier's sodium-based sulfite mill in Hoquiam, Washington. Total capital cost in 1979 dollars is approximately \$3.6 million (\$2.5 million reported).[23] Flow rate of the gas stream from the recovery boiler is about 118 m^3/s (250,000 acfm at 340°F). Effluent SO_2 from the control system has been reduced to less than 1 ppm.[24] The primary control system components are a low-pressure-drop venturi scrubber (1.7 to 2.5 kPa, 7 to 10 in. H_2O) and a crossflow scrubber nucleator.

The reported operating costs were based on the design conditions of operation and the criteria shown in Table 5.6-6.

The emission control system is capable of producing a net annual gain of \$644,000 (\$496,750 reported); the pulp mill, however, is unable to assimilate the full amount of sodium sulfate and heat, and therefore shows a net annual gain of \$169,000 (\$130,000 reported).[24]

In 1976 a calcium-based sulfite mill installed a system for receiving condensed digester blow gases containing SO_2 (42 to 63 g/s, 4 to 6 tons/day average), low-pressure digester gas, and pressure absorber relief gases and sending these gases to the acid plant for SO_2 absorption by the weak cooking acid.[25] The system, installed at a capital cost of \$1.43 million (\$1.16 million reported), includes the following: a 320,000-liter (84,700-gal) stainless steel vessel to receive the gases, sized to accommodate two blows in rapid succession; 284-liter/s (4500-gal/min) heat recovery and 63-liter/s (1000-gal/min) cooler pumps for steam condensation and gas cooling; a 25-liter/s (400-gal/min) heat exchanger feed pump and three heat exchangers to cool the 82°C (180°F) condensate formed during a blow; an eductor and a 95-liter/s (1500-gal/min) eductor feed pump to absorb the cooled SO_2 gases from the digester blow into the weak cooking acid; an additional gas fan between the weak- and strong-acid storage towers to relieve overloading of the existing gas fans; instrumentation that allows operation of the system with no additional manpower; and rehabilitation of an existing deep well for use in cooling raw acid and acid-cooler shower water during summer months.[25] With a few exceptions, this system has eliminated SO_2 discharge (formerly 5 Mg/day [5.5 tons/day]) to the atmosphere from digester blows.[26]

TABLE 5.6-6. CRITERIA AND ANNUAL OPERATING COSTS OF A SULFUR DIOXIDE RECOVERY/CONTROL SYSTEM ON A SODIUM-BASED SULFITE RECOVERY BOILER

Criteria used to determine annual costs	Mid-1979 estimate	Reported - October 1975
Recovered Na_2SO_4	\$104/ton	\$80/ton
Recovered SO_2	\$26/ton	\$20/ton
Electrical cost	\$0.04/kWh	\$0.03/kWh
Steam cost for turbine drive and evaporation	\$1.95/10^6 Btu	\$1.50/10^6 Btu
Recovered thermal value	\$1.30/10^6 Btu	\$1.00/10^6 Btu
Amortization		Straight line--10 yr
Maintenance	1 yr recorded data (less than 1% of capital cost)	1 yr recorded data (less than 1% of capital cost)
Operating manpower	\$19,500/yr	\$15,000/yr
Operating time	8200 h/yr	8200 h/yr
Emission control system capability--financial recovery (700 tons per day)		
Credits/costs	\$/yr	\$/yr
Recovered (credits)		
Na_2SO_4 at average inlet 1 gr/sdcf--4217 tons/yr	437,000	337,000
SO_2 at average inlet 1000 ppm--6841 tons/yr	178,000	137,000
Thermal		
Design 1270 gal/min 55,000,000 Btu/h	585,000	451,000
Total credit	\$1,200,000	\$925,000
Costs		
Electrical power 216 hp 1.6 x 10^6 kWh/yr	62,000	48,000
Steam for turbine fan drive 1200 hp	82,000	63,000
Amortization	207,000	160,000
Maintenance	21,000	16,000
Operation (24 man-hours/wk)	12,000	9,000
Evaporation of water from additional salt formation	171,000	132,000
Total costs	\$555,000	\$428,000

In 1973 a sodium-based sulfite mill (110 Mg/day, 120 tons/day) installed an evaporation, burning, and smelt-handling system. The cost was just over \$3.3 million (\$2 million reported).[27] The primary function of the system is to thicken spent liquor of about 8 percent solids content to 60 percent solids, burn it in a Broby-type furnace, collect the smelt from the furnace bottom, and make smelt flake for sale to kraft mills.[27] Practical processing of the spent liquor in this manner enables the mill to meet effluent standards. The significance of this system for SO_2 control, however, is that an integral part of the system is a two-stage venturi scrubber, the first stage of which is used for SO_2 scrubbing with a weak sodium carbonate solution. The first-stage scrubber recovers SO_2 from three sources--the furnace (in the flue gas), the digester (vent gases), and the acid fortification tower (vent gases).[27]

The principal cost items are the vacuum evaporator, two-stage venturi scrubber (with SO_2 scrubber), modified Broby furnace, and smelt flaker.

In 1973 a calcium-based sulfite pulp mill (191 Mg/day, 100 tons per day) installed a waste sulfite liquor concentration and burning plant similar to that described above for the sodium-based mill, but using direct, triple-effect evaporation. Capital cost was \$3.9 million (\$2.4 million reported).[5] Part of the system is an SO_2 scrubber placed above the direct-contact evaporator, similar to a venturi scrubber. An alkaline solution (sodium carbonate) absorbs SO_2 from the incinerator flue gases. The main components of the system are three vacuum evaporators, an air contact evaporator, a direct-contact evaporator, liquor concentrate tanks, a vertical incinerator, and a cyclone to remove ash from incinerator flue gas.

The only available operating costs are those given earlier in Table 5.6-6.

5.6.2.3 Energy and Environmental Impacts--

Figures on the energy impact of SO_2 removal systems used in the sulfate, sulfite, and neutral sulfite pulping operations are not available. The SO_2 removal systems discussed, however, are not really distinctly constructed as air pollution control methods to reduce SO_2 emissions. The systems are primarily part of the overall chemical recovery systems employed at the mills; thus the energy penalties/credits are intertwined with the other recovery system components (e.g., evaporators, chemical recovery furnace). With respect to the overall recovery system, the sources of energy consumption are pumps, evaporators, recovery furnace, coolers, SO_2 absorption tower recirculation pumps, and fans. The recovery furnace, however, generates steam during the burning of the concentrated waste liquor, which at least partly offsets the energy penalties.

It should be noted that the chemical recovery systems used at pulp mills are inherently water pollution control systems, which eliminate the direct discharge of spent liquor. Many mills, particularly sulfite and NSSC, had to install chemical recovery systems to meet water pollution effluent standards.

The environmental impact with respect to air quality can be viewed differently for pulp mills than for chemical processes installing SO_2 control systems to reduce air pollutants. Because the sulfite process has the greatest potential for emitting SO_2, it will be discussed. When a recovery system is installed at a sulfite mill, a new source of SO_2 emissions is created--the SO_2 absorption towers, which are at the end of the recovery system. The importance of the SO_2 towers, however, is that at many sulfite mills, they operate at high SO_2 removal efficiencies (95 percent plus) and high operability; thus it is an important SO_2 control technique.

Table 5.6-3 shows typical SO_2 emissions (per megagram and ton of air-dried pulp) from sulfite mill sources. The impact of an uncontrolled recovery process would be great (80 to 250 kg/Mg, 160 to 500 lb/ton), but would not be run uncontrolled because the loss of SO_2 would mean a loss in sulfite/bisulfite chemical recovery. Operabilities and reliabilities of several sulfite mills reported in one study were 100 percent.[28] The absorption towers are normally overhauled during scheduled pulp mill shutdowns. Mills usually have a certain capacity for storing liquor in the event an SO_2 absorption system must temporarily shut down for repairs.

Controlled emissions from the recovery process as shown in Table 5.6-3 are 6 to 20 kg/Mg (12 to 40 lb/ton) of air-dried pulp.[10] The same report, showing SO_2 system operabilities and reliabilities, also shows the outlet concentrations (from the absorbers) from six sulfite mills. The average concentration from the towers is approximately 225 ppm with a range from 60 (calculated from reported SO_2 values) to 400 ppm.[10]

The pulp mill recovery system may be best summarized as a "controlled source." Although a source of SO_2 emissions, the absorption towers at reported mills have been very efficient in removing SO_2. The scrubber products are not disposed of in the environment, but are recycled to the pulping process.

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5.7 COAL MINING WASTE DISPOSAL

5.7.1 Process Descriptions and Emission Sources

The mechanized extraction of coal from the mine and its preparation at the plant by current mechanized mining methods generate large quantities of waste to be disposed of. The principal problems associated with coal waste disposal are pollution of air and water, nonproductive use of land, and loss of aesthetic value. Landslides are another potential problem.[1]

Coal mining waste (including "coal refuse", "culm", and "gob") consists primarily of a mixture of coal, rock, carbonaceous shales, and pyrites (FeS_x).[1] These rejected materials may amount to 20 percent or more of the tonnage mined.[1] Coal mining waste has no immediate use and is disposed of as economically and conveniently as possible. The most common practice has been simple open-end dumping of the mining waste in piles or banks. In Appalachia, the waste is usually disposed in hillside dumps, valley fills, or earthen dams. Dumptrucks, conveyor belts, mine cars, and aerial tramways are used to move the waste material from the mine to the disposal site.[1]

Disposal sites for coal mining waste often become dumping grounds for other discarded items such as grease-soaked rags, grease and oil containers, trash and garbage from nearby homes, wood, and other combustible organic matter. Depending on the age of a pile and the local mining and preparation methods, the combustible content can vary from 10 to 60 percent.[2]

Until recently, coal mining waste piles commonly burned or smoldered continuously, sometimes for years, releasing noxious gases and particulate matter into the atmosphere. Fortunately there is growing evidence that the number of actively burning piles is steadily diminishing, as shown in Table 5.7-1. Most of these piles are located in Virginia, West Virginia, Pennsylvania, and Kentucky,[3] and are believed to be confined largely to older waste banks.[4]

TABLE 5.7-1. ACTIVELY BURNING COAL MINING WASTE PILES IN THE UNITED STATES[3,5,6]

Year	Number
1964	495
1968	292
1972	206

Spontaneous combustion is probably the major cause of coal mining waste fires, although some are caused by lightening; grass, brush, or forest fires; trash fires; and intentional ignition to create "red dog" residue for road base or other foundation purposes.[5,6] Spontaneous ignition is influenced by the temperature, the coal rank, and the pyrite, moisture, and oxygen content of the pile. These factors in turn depend on rainfall and windspeed, and on the particle size distribution, void ratio, and surface characteristics of the pile. If the waste pile is porous because of improper layering and compaction, water and air can infiltrate deep within the mass. Organic and pyritic materials become oxidized and release heat. The trapped heat builds up within the pile, leading eventually to auto-ignition.

Air pollutants released from burning or smoldering coal mining waste banks include sulfur oxides (SO_x), hydrogen sulfide (H_2S), sulfuric acid (H_2SO_4), nitrogen oxides (NO_x), ammonia (NH_4), carbon monoxide (CO), hydrocarbons, and particulates. Sulfur dioxide is formed by thermal decomposition and oxidation of pyritic material (FeS_x) in the refuse:

$$FeS_2 + 3O_2 \rightarrow FeSO_4 + SO_2.$$

Sulfuric acid, produced through the reaction

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4$$

can react with pyritic material to form H_2S:

$$H_2SO_4 + FeS \rightarrow FeSO_4 + H_2S.$$

Hydrogen sulfide is also likely to be formed by a number of other possible reactions. Elemental sulfur, often observed on the surface of burning piles, is formed by the thermal breakdown of the pyrite FeS_2, or by the reaction of hydrogen sulfide and SO_2:

$$2H_2S + SO_2 \rightarrow 3S + 2H_2O.$$

Estimates of atmospheric SO_2 emissions from burning coal mining waste piles have been variable. In 1968 it was estimated that 0.54 Tg (600,000 tons) was emitted annually.[7] In 1970 the EPA estimate was 0.128 Tg (141,000 tons) of SO_x emitted to the atmosphere from 245 Tg (270 million tons) of burning coal mining wastes.[8] More recent estimates place the annual national SO_2 emission from such sources at 0.039 Tg (43,000 tons) per year.[9] The latter estimate may be the most accurate because the number of actively burning piles is believed to be decreasing and also because the estimate assumes that only 21 percent of the available refuse mass is burning.

Air samples taken from communities near burning coal mining waste piles were reported in 1971 to contain, on the average, more than 1 ppm SO_2, with peak concentrations exceeding 4.5 ppm.[5] Hydrogen sulfide concentrations exceeding 0.4 ppm have also been measured.[10]

5.7.2 Control Techniques

The control of SO_x and other air emissions from coal mining waste piles involves prevention and extinguishment of fires.

Proper layering and compaction are the two principal techniques used in newer coal mining waste banks to prevent fires.[11] Because these methods significantly reduce the permeation of air and water into the waste mass, spontaneous fires seldom occur.[5] In addition to layering and compaction, the following preventive measures are important.

- Proper selection and preparation of the disposal site: The ideal site has flat terrain. In mountainous regions, valleys and hillsides are used. The site should be close to an adequate supply of noncombustible material to be sandwiched between refuse layers and compacted or sealed around the sides to prevent air infiltration. Cross-valley fills should be avoided.[12] All vegetation is removed.[13,14]

- Optimum refuse bank design: Side dumps are less likely to ignite than end dumps. Exposed surface area is minimized. Terracing reduces fire hazard by checking the draft along a slope. Slopes of 50 percent or less are recommended.[13]

- Removal of combustible organic materials: Dumping of grease rags, domestic garbage, vegetation, and the like is prohibited. Carbonaceous content of the coal waste is reduced, if possible, by improvement in coal preparation techniques.

- Increased percentage of fines: A maximum of 15 percent fines improves compaction and impermeability of the waste mass.[15]

- Water flow: Ground, surface, and runoff waters are avoided or diverted to prevent heat generation from infiltration of the waste mass, and also to prevent water pollution.

- Sealing: Clay or dirt is used to seal exposed edges of the pile to prevent air and water infiltration, which lead to heat buildup inside the pile.
- Fencing and posting: These practices minimize the possibility of ignition by trespassers.
- Reclamation: Vegetation is planted to finish the pile, both to prevent erosion and to enhance aesthetic effects.

The following methods have been developed to control burning coal mining waste piles.[16]

- Blanketing: The top and sides are sealed with fly ash, clay, dirt, quarry wastes, polyurethane foam, or other noncombustible material to restrict the flow of air into the burning piles. The effectiveness of this blanketing or smothering generally is limited because the seal eventually weathers and cracks to become ineffective over hot spots.
- Spraying/sprinkling: Water is sprayed over the entire bank. This is only a temporary solution, because the pile reignites once the sprinkling stops.
- Isolation: Trenches are dug to isolate the hot area from the rest of the culm. The burning area is then quenched with water or is blanketed.
- Grouting: A slurry of water and pulverized limestone, fly ash, coal silt, or sand is injected by force into the burning pile to cool the mass and fill voids.
- Use of explosives: Explosives are placed deep within a burning pile by drilling horizontal holes. The explosion creates fissures in the hard, crusty, clinker surface of the pile so water can penetrate and quench the fire.
- Accelerated combustion and quenching: Burning refuse is lifted, then dropped 15 to 30 meters (50 to 100 ft) through the air into a lagoon. The fall rapidly burns combustible material and the water quenches the heat. The principal disadvantage is generation of particulates while the burning mass is falling.
- Cooling and dilution: Water-cooled waste is mixed by bulldozer with soil and old burned-out waste, then compacted.
- Hydraulic jets: High-velocity water cannons quench burning waste, which is then compacted.

Further details are available regarding prevention and control of coal mining waste fires.[17,18,19]

5.7.2.1 Control Costs--

Information on the cost of controlling SO_x emissions from coal mining waste piles is limited. No cost information is available in the literature concerning SO_x emission control through fire preventive design of coal waste piles. Table 5.7-2 presents cost information relative to the methods used to extinguish coal mining waste fires. Hauling and repiling extinguished material by tractor-scraper may be less expensive than using bulldozers because of the elimination of a material handling step.[20] Fire extinguishing techniques utilizing water appear to be considerably less expensive than other techniques using grouting, foam blanketing, or explosive materials.

5.7.2.2 Energy and Environmental Impact--

As noted earlier, methods for extinguishing coal mining waste fires with water are relatively inexpensive and are frequently used. The application of large volumes of water to the burning mass results in runoff, which often is contaminated with acids, metals, and other pollutants requiring neutralization and sedimentation treatment. Obviously, methods that do not involve using water, such as blanketing or sealing, do not lead to water pollution problems. Fire preventive methods that prevent the infiltration of water into the coal mining waste pile will help prevent pollution of ground and surface runoff waters. Examples of such preventive methods are layering, compaction, sealing, and revegetation.

TABLE 5.7-2. RELATIVE COSTS OF DEMONSTRATED METHODS OF EXTINGUISHING COAL MINING WASTE FIRES[16,20,21]

Method	Cost per cubic meter, $ July 1979
Blanketing/sealing	
Polyurethane foam	4.37 (1971 or earlier)
Clay	
Sand	
Limestone	
Explosives	2.86 (1968) 2.85 (prior to 1971)
Grouting	
Lime slurry	1.46 (1969)
Lime/limestone slurry followed by limestone seal	1.63 (1971 or earlier)
Ponding	
Water monitors and lagoons	0.92-1.35 (prior to 1971)
Spraying	
Quenching, bulldozers, and drag lines	1.48 (1971 or earlier)
Water sprinkling, dozer digout with repile in compact layers	0.86 (1971 or earlier)
Cooling and dilution	0.60 (1968)
Quenching, hauling by tractor-scraper	0.57 (1970)
Hydraulic jets	0.98 (1968) 0.86 (1970)
Isolation	
Trenching followed by quenching or blanketing	
Digging out and spreading	
Accelerated combustion and quenching	

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5.8 GLASS MANUFACTURE

5.8.1 Process Descriptions and Emission Sources

5.8.1.1. Introduction--

The glass manufacturing industry is made up of several different segments, classified by the Standard Industrial Classification (SIC) System as shown in Table 5.8-1. In early 1978, 129 primary glass producing companies operated 338 plants, most located east of the Mississippi River.[1] In 1976 the industry produced nearly 17 Tg (19 million tons) of glass, most of which was soda-lime glass.[2] The reported value of glass shipments that year was over 6 billion dollars. Table 5.8-1 gives further details.

On a nationwide basis, the glass industry is estimated to be responsible for 0.1 percent of total annual SO_x emissions.[3] Historically, this industry has maintained compliance with applicable SO_x regulations through process control techniques such as batch sulfur control and fuel selection; add-on SO_x emission control devices have generally not been used.

5.8.1.2 Process Description--

Temperatures ranging from 1500° to 1700°C (2732° to 3092°F) are used to convert inorganic oxides of silicon (SiO_2), sodium (Na_2O), calcium (CaO), and other elements to liquid mixtures that, after cooling, are homogeneous, amorphous, multicomponent, and often transparent; such mixtures are known generically as glass. More than 50 different glass compositions are available, but soda-lime glass reportedly accounts for 90 to 95 percent of all the glass produced.[2,4] The finished composition of soda-lime glass is typically 70 to 74 percent SiO_2, 10 to 13 percent CaO, and 13 to 16 percent Na_2O.[5] It is used to make flat glass (such as windows), container glass (such as food, beverage, and drug containers), and pressed and blown glass (tableware, tubing, and light bulbs).

Sand, soda ash, and limestone are the major raw materials used in soda-lime glass manufacture. Cullet (ground and recycled glass) is used as makeup material and may contribute 10 to 50 percent or more of the finished product.[6,7] Other ingredients are considered minor because they generally constitute 5 percent or less of the material mixed in a batch. Table 5.8-2 gives further information about the raw materials used in manufacturing soda-lime glass.[8-11]

TABLE 5.8-1. GLASS MANUFACTURING INDUSTRY[2]

Industry segment	SIC code	Number of plants in 1978	Production in 1976, Tg (million tons)	Value of 1976 shipments, millions of dollars
Flat glass, including sheet, plate and float, laminated, and tempered automobile glass	3211	32	2.56 (2.91)	645
Container glass, including food, beverage, and pharmaceutical glass	3221	117	11.80 (13.00)	3251
Pressed and blown glass, including tableware, television tubes, light bulbs, lamp enclosures, tubing, and textile fiberglass	3229	165	1.73 (1.95)	1598
Wool fiberglass	3296	24	0.896 (0.986)	817
Total		338	16.976 (18.846)	6311

TABLE 5.8-2. RAW MATERIALS USED IN MANUFACTURING SODA-LIME GLASS[8-11]

Ingredient	Purpose	Amount of ingredient mixed in batch, weight %
Major components		
Glass sand (>99% SiO_2)	Provides SiO_2	60-70
Soda ash (Na_2CO_3)	Provides Na_2O, the primary agent for fluxing or lowering of the melting point	17-20
Limestone or burnt lime from dolomite ($CaCO_3$, $MgCO_3$)	Provides CaO and MgO	7-15
Minor components		
Feldspars ($Na_2O/K_2O \cdot Al_2O_3 \cdot 6SiO_2$) or nepheline syenite ($Na_2O \cdot 1.7Al_2O_3 \cdot 4SiO_2$)	Provide AlO_3 to lower melting point and add stability to the glass by retarding devitrification; other ingredients are glass forming oxides	0-6
Fining agents		
Sulfates (Na_2SO_4, $BaSO_4$, or $[NH_4]_2SO_4$	Help in reduced sulfite form to condition glass; bubbles are removed from the molten glass by gas evolution	0.5-5
Peroxides; nitrates; chlorates; chloride salts; arsenic, cerium and manganese oxides; and other chemicals	Help to condition glass by removing bubbles through gas evolution or evaporation	<1
Powdered coal	Provides carbon for reducing sulfates to sulfite form	<1
Coloring and decolorizing agents (many metallic oxides, selenium)	Add or remove color from glass	<1
Oxidizing agents (KNO_3, $NaNO_3$)	Oxidize iron contaminants to make them less visible	<1

Typically, 540 kg (1200 lb) of raw material is needed to produce 454 kg (1000 lb) of container glass, 90 percent of which is salable.[4] The remainder is recycled as cullet. About 18 percent of the raw material fed to the furnace is given off as gas, most of which is carbon dioxide (CO_2).[12] For each kilogram (2.2 lb) of raw material that is lost, over 2 m^3 (70 ft^3) of off-gas is created at 1500°C (2732°F).[12] Finished glass occupies less than half of the volume of the unmelted raw materials.[12]

The chemical reactions involved in soda-lime glass manufacture are as follows:[6]

$$Na_2CO_3 + xSiO_2 \xrightarrow{\Delta} Na_2O \cdot xSiO_2 + CO_2\uparrow$$

$$CaCO_3 + ySiO_2 \xrightarrow{\Delta} CaO \cdot ySiO_2 + CO_2\uparrow$$

$$C + Na_2SO_4 + zSiO_2 \xrightarrow{\Delta} Na_2O \cdot zSiO_2 + SO_2\uparrow + CO\uparrow$$

The last reaction may take place in two steps:

$$Na_2SO_4 + C \rightarrow Na_2SO_3 + CO\uparrow$$

$$Na_2SO_3 + zSiO_2 \xrightarrow{\Delta} Na_2O \cdot zSiO_2 + SO_2\uparrow$$

Carbon dioxide may also form according to the following reaction:

$$2Na_2SO_4 + C \rightarrow 2Na_2SO_3 + CO_2\uparrow$$

Figure 5.8-1 is a typical flow diagram for the manufacture of soda-lime glass; steps in the production of other types of glass resemble those for soda-lime glass. The major and minor ingredients are premixed and stored in hoppers until charged to the furnace, where temperatures generally ranging from 1500° to 1700°C (2732° to 3092°F) convert the mixture into a molten mass. The mass is held until it is of uniform consistency and until refining (the process of removing gas bubbles, such as CO_2, H_2O, and SO_2) is complete. The temperature is slowly lowered to about 1300°C (2372°F) to increase the viscosity and to condition the melt for the next processing steps forming.[13]

In the forming and finishing processes, the molten glass is extracted from the furnace, shaped to the desired form, and annealed within a specific temperature range. The final product is either inspected and shipped or sent for further finishing, such as tempering or decorating. Rejected product is crushed and recycled as cullet.

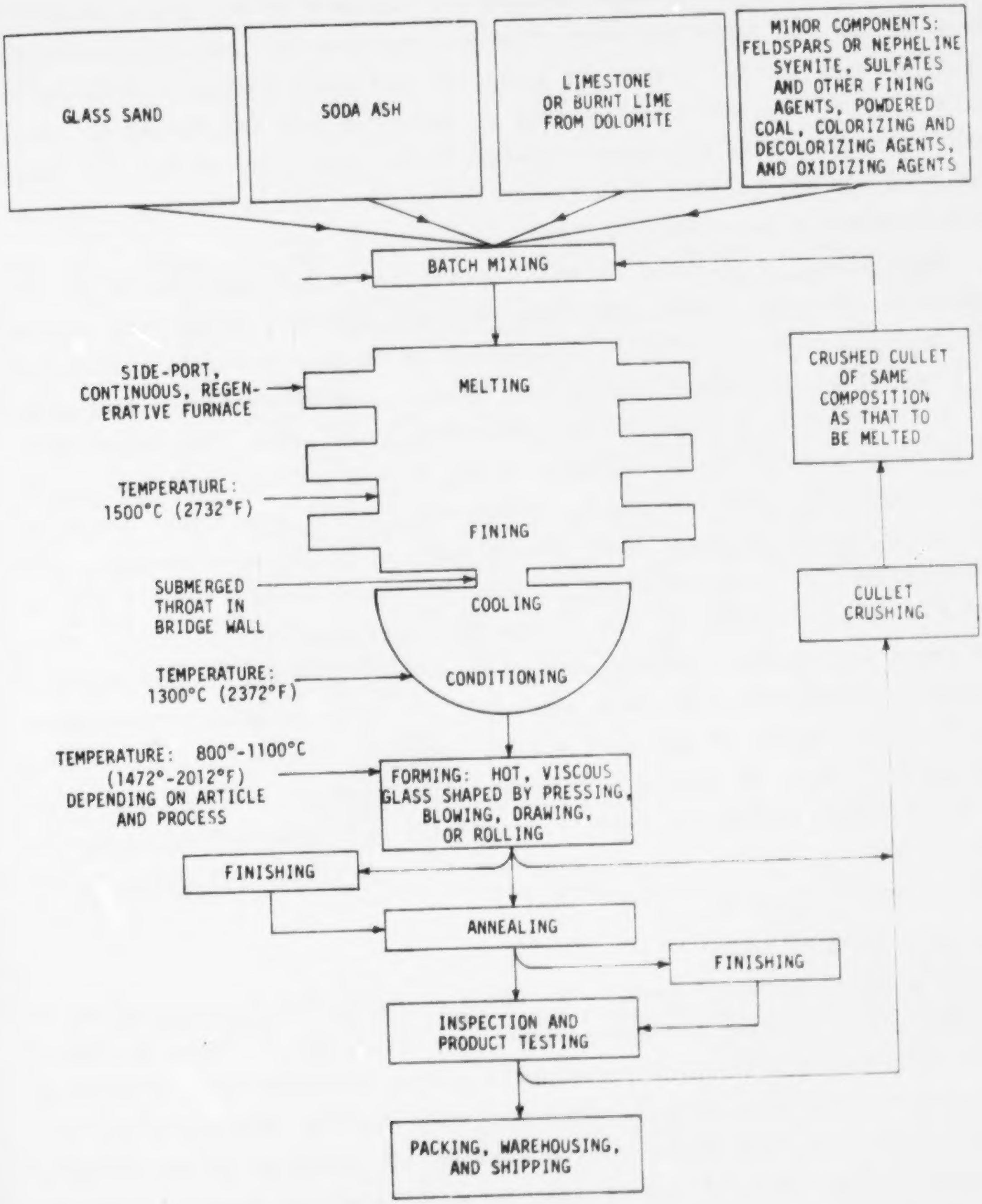
GLASS SAND
SODA ASH
LIMESTONE OR BURNT LIME FROM DOLOMITE
MINOR COMPONENTS: FELDSPARS OR NEPHELINE SYENITE, SULFATES AND OTHER FINING AGENTS, POWDERED COAL, COLORIZING AND DECOLORIZING AGENTS, AND OXIDIZING AGENTS
BATCH MIXING
SIDE-PORT, CONTINUOUS, REGENERATIVE FURNACE
MELTING
TEMPERATURE: 1500°C (2732°F)
FINING
SUBMERGED THROAT IN BRIDGE WALL
COOLING
TEMPERATURE: 1300°C (2372°F)
CONDITIONING
TEMPERATURE: 800°-1100°C (1472°-2012°F) DEPENDING ON ARTICLE AND PROCESS
FORMING: HOT, VISCOUS GLASS SHAPED BY PRESSING, BLOWING, DRAWING, OR ROLLING
FINISHING
ANNEALING
FINISHING
INSPECTION AND PRODUCT TESTING
PACKING, WAREHOUSING, AND SHIPPING
CRUSHED CULLET OF SAME COMPOSITION AS THAT TO BE MELTED
CULLET CRUSHING

Figure 5.8-1. Typical flow diagram for the manufacture of soda-lime glass.[14]

Both batch and continuous furnaces are operated in the glass industry. Day pots and day tanks are used if only a few tons or less of a specialty glass, such as optical glass, art glass, or cast plate glass, is produced.[15] Day pots are made of selected clay or platinum and are heated to about 1400°C (2552°F) in multiple-pot furnaces;[16] the capacities of day pots range from 9 kg (20 lb) to 1800 kg (2 tons).[17] Day tanks are refractory lined and can hold somewhat more than day pots.

Most glass is produced in continuously operating regenerative or recuperative furnaces. The capacities of these furnaces range from 0.9 to 1350 Mg (1 to 1500 tons).[15],[16] A regenerative furnace generally consists of two chambers of refractory, called checkerwork. While combustion flue gases heat the refractory in one checkerwork chamber, the other checkerwork chamber preheats combustion air. Every 10 to 30 minutes the gas flow is reversed, combustion air is drawn through the chamber previously heated by flue gases, and flue gases heat the refractory in the other chamber. The firing pattern of a regenerative furnace can be end-port (Figure 5.8-2) or side-port (Figure 5.8-3).[18] These furnaces are operated continuously for 4 to 5 years at sustained temperatures up to 1600°C (2900°F).[19] When operated at lower temperatures, additional furnace life can be expected. A recuperative furnace consists of one continuously operating shell with tubular heat exchangers instead of checkerwork heat exchangers to preheat combustion air.[20] Furnace combustion heat is recovered and transferred to cooler incoming air by passing the incoming air through pipes surrounded by the outgoing combustion gases.

5.8.1.3 Emission Sources--

Table 5.8-3 presents annual SO_x emission rates for the production of container glass, pressed and blown glass, and flat glass.[21] Rates estimated in the 1976 source assessment documents are less than the rates obtained by site testing from June 1976 to September 1978 for the production of container glass and flat glass. Site testing of container glass furnaces primarily firing fuel oil showed that in most cases the emission rate for SO_x was higher than for any other criteria pollutant in the production of container glass. Table 5.8-4 summarizes emission data from EPA site testing,[22] Table 5.8-5 presents SO_x emission data provided by industry,[23] and

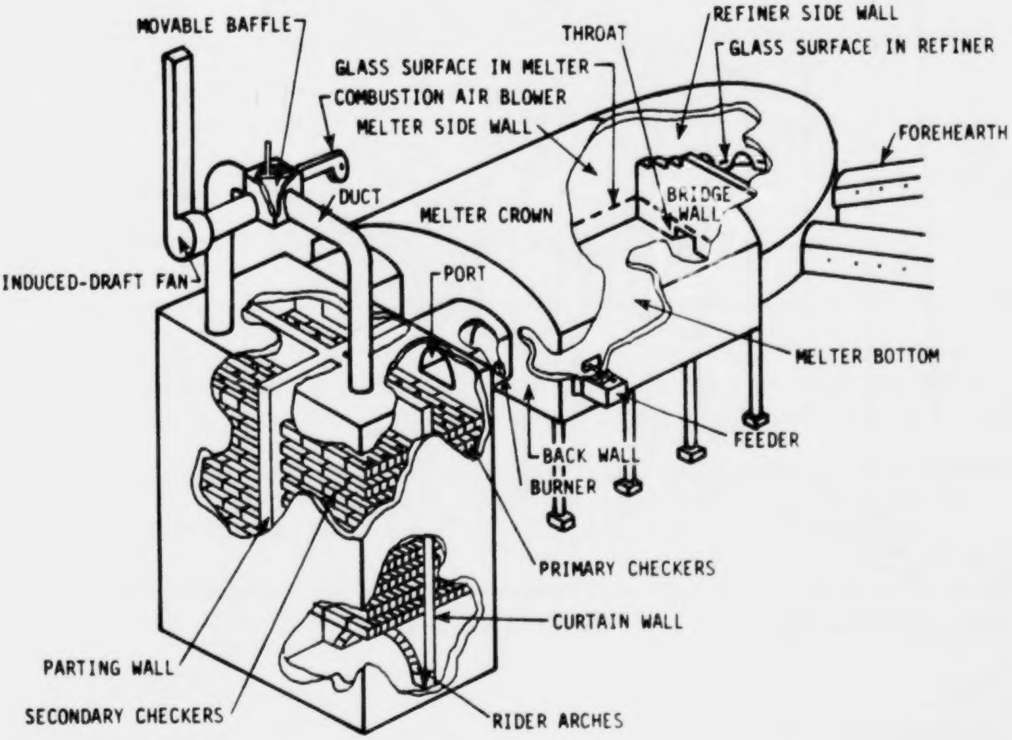
MOVABLE BAFFLE
THROAT
REFINER SIDE WALL
GLASS SURFACE IN REFINER
GLASS SURFACE IN MELTER
COMBUSTION AIR BLOWER
MELTER SIDE WALL
FOREHEARTH
DUCT
BRIDGE WALL
MELTER CROWN
INDUCED-DRAFT FAN
PORT
MELTER BOTTOM
FEEDER
BACK WALL
BURNER
PRIMARY CHECKERS
CURTAIN WALL
PARTING WALL
SECONDARY CHECKERS
RIDER ARCHES

Figure 5.8-2. End-port continuous regenerative furnace.[18]

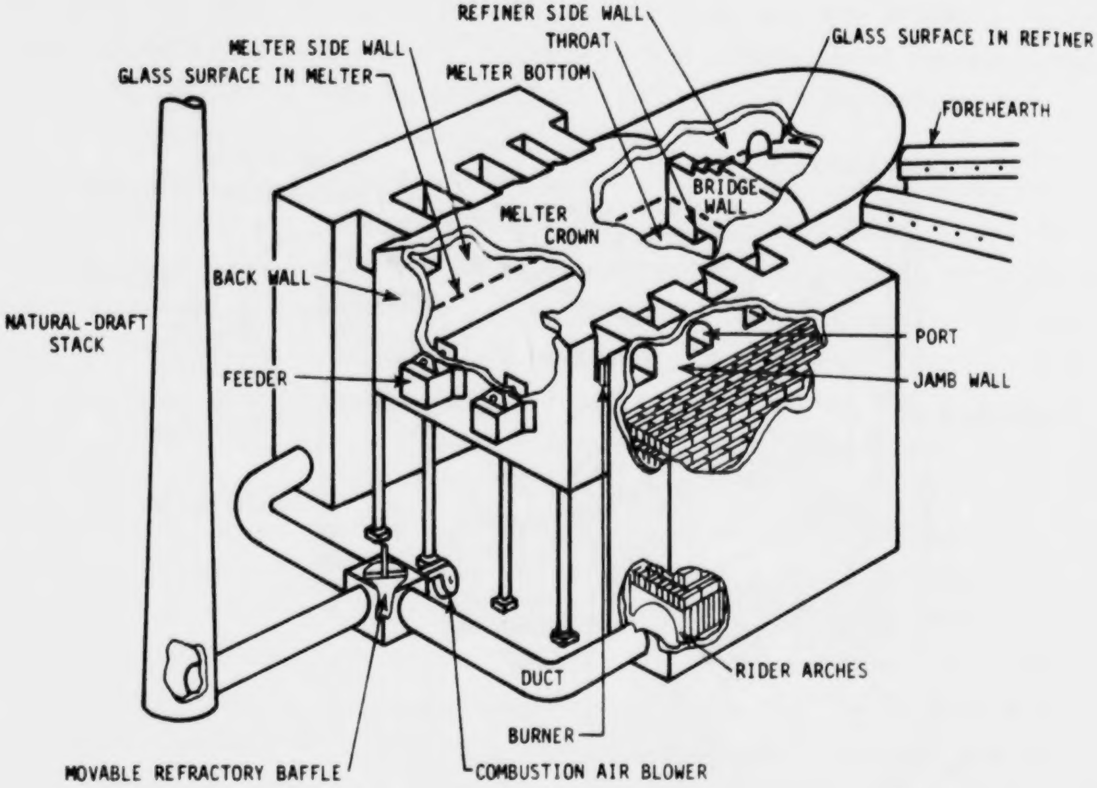
REFINER SIDE WALL
MELTER SIDE WALL
THROAT
GLASS SURFACE IN REFINER
GLASS SURFACE IN MELTER
MELTER BOTTOM
FOREHEARTH
BRIDGE WALL
MELTER CROWN
BACK WALL
NATURAL-DRAFT STACK
PORT
FEEDER
JAMB WALL
DUCT
RIDER ARCHES
BURNER
MOVABLE REFRACTORY BAFFLE
COMBUSTION AIR BLOWER

Figure 5.8-3. Side-port continuous regenerative furnace.[18]

TABLE 5.8-3. ESTIMATES OF ANNUAL SO_x EMISSIONS FROM GLASS MANUFACTURE [Mg/yr (tons/yr)] [21]

Source of data	Container glass[a]	Pressed and blown glass[b]	Flat glass[c]
EPA source assessment documents, 1976	72-111 (80-123)	51 (56)	349 (380)
EPA site testing, 1976 to 1978	200-342 (220-380)	0-31 (0-34)	597 (630)

[a] EPA Source Assessment Document data derived from 46 flint container glass furnaces that were probably all gas-fired. Site testing data derived from 8 container glass plants, 6 of which burned oil, and 2 gas.

[b] EPA Source Assessment Document data derived from 5 pressed and blown furnaces. Site testing data from 2 pressed and blown borosilicate, 1 pressed and blown lead, and 1 pressed and blown soda-lime furnace.

[c] EPA Source Assessment Document Data derived from 5 flat glass furnaces. Site testing data from 1 soda-lime flat glass furnace.

TABLE 5.8-4. EMISSION DATA FROM SITE TESTING[22]

Type of glass produced	Process rate, kg/h (lb/h)	Fuel (sulfur content unknown)	SO_x, kg/h (lb/h)	Kg SO_x/Mg glass produced (lb/ton)
Container glass-soda-lime	5,470 (12,058)	No. 6 oil	16.21 (35.7)	2.45 (5.95)
Container glass-soda-lime	8,391 (18,499)	No. 6 oil	24.3 (53.6)	2.38 (5.79)
Container glass-soda-lime	6,227 (13,728)	No. 6 oil	23.8 (52.3)	3.14 (7.62)
Container glass-soda-lime	5,162 (11,380)	No. 6 oil	53.35 (117.6)	8.51 (20.67)
Container glass-soda-lime	5,384 (11,871)	No. 6 oil	54.10 (119.3)	8.28 (20.12)
Container glass-soda-lime	7,274 (16,039)	No. 2 oil	11.3 (25.0)	1.29 (3.12)
Pressed and blown-borosilicate	950 (2,094)	No. 2 oil	2.2 (4.8)	1.88 (4.57)
Container glass-soda-lime	9,873 (21,767)	Gas	25.21 (55.57)	2.09 (5.11)
Container glass-soda-lime	11,204 (24,701)	Gas	39.22 (86.46)	2.88 (7.00)
Pressed and blown-soda-lime	1,657 (3,653)	Gas	0.46 (1.013)	0.23 (0.55)
Pressed and blown-borosilicate	931 (2,053)	Gas	<0.1 (<0.1)	<0.04 (<0.1)
Pressed and blown-lead	811 (1,789)	Gas	0.10 (0.21)	0.09 (0.23)
Flat glass-soda-lime	15,876 (35,000)	Gas	68.20 (150.3)	3.54 (8.58)

TABLE 5.8-5. SUMMARY OF SO_x EMISSION DATA SUPPLIED BY GLASS MANUFACTURERS[23]

Type of glass	Fuel	SO_x emitted, kg/hr (lb/hr)	SO_2 emitted, kg/Mg (lb/ton)
Container			
Amber		a	5.1 (10.2)[b]
Flint		a	0.6 (1.2)[b]
Soda-lime			
Pressed and blown			
Soda-lime	Gas and boost	10.48 (23.1)	a
Soda-lime	No. 2 oil and boost	52.94 (116.7)	a
Borosilicate	No. 2 oil	5.49 (12.1)	a

[a] Value cannot be calculated from available data.

[b] Values are derived by difference, based upon batch input and retention of sulfur. They assume a fuel with no sulfur content. The total SO_2 emission will be a function of fuel sulfur content.

Table 5.8-6 gives emission factors for glass manufacturing procedures.[24]

It should be noted that emissions from container glass furnaces and their pattern of fuel usage are disproportionately represented in the site testing data in Table 5.8-4. Six out of eight (75 percent) of the container glass furnaces tested burned fuel oil, but fuel usage statistics for the container glass segment of the industry indicate that only one out of five burns fuel oil.[25]

The major source of SO_x emissions in the glass industry is the glass melting operation. Forming and annealing operations are minor sources. Furnace emissions appear to be attributable to both the manufacturing process and the fuel burned, the latter being the predominant source (at least in the pressed and blown segment of the industry).[26] Fuel-derived SO_x emissions are lower from natural-gas-fired furnaces than from oil-fired furnaces, unless the oil has been desulfurized.[27] Flue gases from furnaces burning natural gas have been reported to contain 2 ppm SO_x or less.[23] Roughly 600 ppm SO_x can be expected in flue gas from a furnace burning fuel oil containing 1 percent sulfur.[28] The SO_x emissions from glass manufacturing would be expected to increase with increased use of fuel oil. Greater use of electric furnaces or electric boosting, however, may decrease SO_x emissions.

Process-derived SO_x emissions come from sulfur compounds such as sodium sulfate (salt cake) used to condition glass, as in the manufacture of soda-lime glass and wool fiberglass. The greater the sulfur content of the raw batch, the higher the SO_x emissions.[27] About 40 percent of the sulfur added as sulfate is vaporized and exhausted as gaseous SO_x or condensed sodium sulfate.[27]

The vaporization of sulfur compounds involves several reactions. Sulfur dioxide is released when sodium sulfate chemically reacts with the melt.[29]

$$Na_2SO_4 + xSiO_2 + C \rightarrow Na_2O \cdot xSiO_2 + CO\uparrow + SO_2\uparrow$$

At the same time, sulfur trioxide may be produced from the thermal decomposition of sodium sulfate.

$$Na_2SO_4 \xrightarrow{\Delta} Na_2O + SO_3\uparrow$$

TABLE 5.8-6. EMISSION FACTORS FOR GLASS MANUFACTURING PROCEDURES[a,b,c]

	SO_x	
	Kg/Mg	lb/ton
Raw material handling[d]	0	0
Melting furnace[e]		
Container glass		
Uncontrolled	1.7(1.0-2.4)	3.4(2.0-4.8)
With low-energy scrubber[f]	0.9	1.7
With venturi scrubber[g]	0.1	0.2
With fabric filter	1.7	3.4
With electrostatic precipitator	1.7	3.4
Pressed and blown glass		
Uncontrolled	2.8(0.5-5.4)	5.6(1.1-10.9)
With low-energy scrubber[f]	1.3	2.7
With venturi scrubber	0.1	0.3
With fabric filter	2.8	5.6
With electrostatic precipitator	2.8	5.6
Flat glass		
Uncontrolled	1.5(1.1-1.9)	3(2.2-3.8)
With low-energy scrubber[f]	0.8	1.5
With venturi scrubber[g]	0.1	0.2
With fabric filter	1.5	3.0
With electrostatic precipitator	1.5	3.0

[a] Source: Reference 24.

[b] Emission factors are expressed as grams of SO_x per kilogram of glass produced and as pounds of SO_x per ton of glass produced.

[c] When literature references report ranges in emission rates, these ranges are shown in parentheses along with the average emission factor. Single emission factors are averages of literature data for which no ranges are reported.

[d] Emission factors for raw materials handling are not separated into types of glass produced because batch preparation is the same for all types. Particulate emissions are negligible because almost all plants utilize some form of control (i.e., fabric filters, scrubber, or centrifugal collectors).

[e] Control efficiencies for the various devices are applied only to the average emission factor.

[f] Approximately 52 percent efficient in reducing particulate and sulfur oxide emissions.

[g] Approximately 95 percent efficient in reducing particulate and sulfur oxide emissions.

In the vapor state over the melt, sulfur dioxide may be oxidized to form additional sulfur trioxide.

$$SO_2 + 1/2O_2 \rightarrow SO_3\uparrow$$

Vapors over the melt may recombine to form sodium sulfate.

$$Na_2O + H_2O \xrightarrow{1000°C} NaOH$$

$$2NaOH + SO_3 \xrightarrow{1000°C} Na_2SO_4\uparrow + H_2O\uparrow$$

As the temperature in the exhaust stack falls to about 200°C (400°F), the rising vapors condense as fine, usually submicrometer particulates. Sodium sulfate has been found to be the major component of particulate emissions from soda-lime glass manufacture; 75 percent of these particulate emissions are less than 1 micrometer in diameter.[29]

5.8.2 Control Techniques

5.8.2.1 Description--

Essentially all of the SO_x emitted during glass manufacture is generated in the melting process. Glass furnace emissions can be reduced by three means: process modifications, fuel changes, and add-on control equipment.

Process modifications that may reduce SO_x emissions include altering the raw material charge to reduce the sulfur content or to increase the fraction of recycled glass, changing the furnace controls or equipment, and altering the pull rate. Process modifications that reduce the salt cake content in the raw batch can significantly reduce SO_x emissions. For example, one California flat-glass plant reportedly reduced furnace emissions of SO_2 by 78 percent from 2.1 to 0.5 kg/Mg (5.0 to 1.1 lb/ton) by reducing the salt cake in the raw batch 60 percent (from 12 to 5 kg/Mg, 30 to 12 lb/ton of sand).[30] Similarly, another California flat-glass plant has reportedly reduced its SO_2 emissions 75 percent (from 1.6 to less than 0.4 kg/Mg, 4 to less than 1 lb/ton of batch constituents) by reducing the input of salt cake. Glass quality was not compromised in either case.[31] The salt cake cannot be reduced below certain minimums without effecting glass quality. The minimum salt cake required varies depending upon furnace type, pull rate, glass type, and other variables.

Fuel changes have also been shown to reduce SO_x emissions. These include switching to natural gas or low-sulfur fuel oil, switching to all-electric melting, and using electric boosting for melting. Electric melters significantly reduce SO_x, NO_x, and particulate emissions because they eliminate the combustion of fossil fuels. Electric melting also is reported to minimize SO_x and other gaseous losses from the vaporization of raw materials because the surface of the melt is insulated by a semisolid crust. Gases discharged through the crust of the melt consist mainly of carbon dioxide and water.[33] Today, borosilicate, opal, and green glass are produced with electric furnaces.[34] The capacities of such furnaces are about 100 to 110 Mg/day (110 to 120 tons/day). Electric melters have not been demonstrated for larger operations, such as large container furnaces, the nominal capacities of which are about 220 Mg/day (240 tons/day), and flat-glass furnaces, which range from about 600 to 800 Mg/day (660 to 880 tons/day).[35]

Several emission control systems that are available to the glass industry for particulate control are also capable of achieving various levels of secondary SO_x control. For example, a venturi scrubber system of the type shown in Figure 5.8-4 can control SO_x emissions from commercial glass plants.[36] As shown, the system includes a packed tower where part of the sulfate particulates are removed from the hot furnace flue gases, a dual-throat venturi scrubber where SO_2 and additional particulates are removed by alkaline washing, and a cyclone for final particulate collection. A pilot system of this type at a glass furnace in early 1973 achieved SO_2 control efficiencies as high as 90 percent.[37] Similar full-scale systems have reduced SO_2 emissions 75 to 90 percent.[38] Specific parameters for these systems are given in Table 5.8-7. Currently, only the container glass segment of the glass industry is reported to use scrubber systems for emission control.[39]

Electrostatic precipitators (ESP's) and fabric filters appear to be of limited use for SO_x control. One company reports an SO_2 emission reduction of 15 percent and SO_3 emission reduction of 40 percent with an ESP, but such effects have not been noted in other ESP tests.[40]

Injecting a sorbent such as alumina, limestone, or nepheline syenite into a fabric filter system can effectively remove SO_x from furnace flue

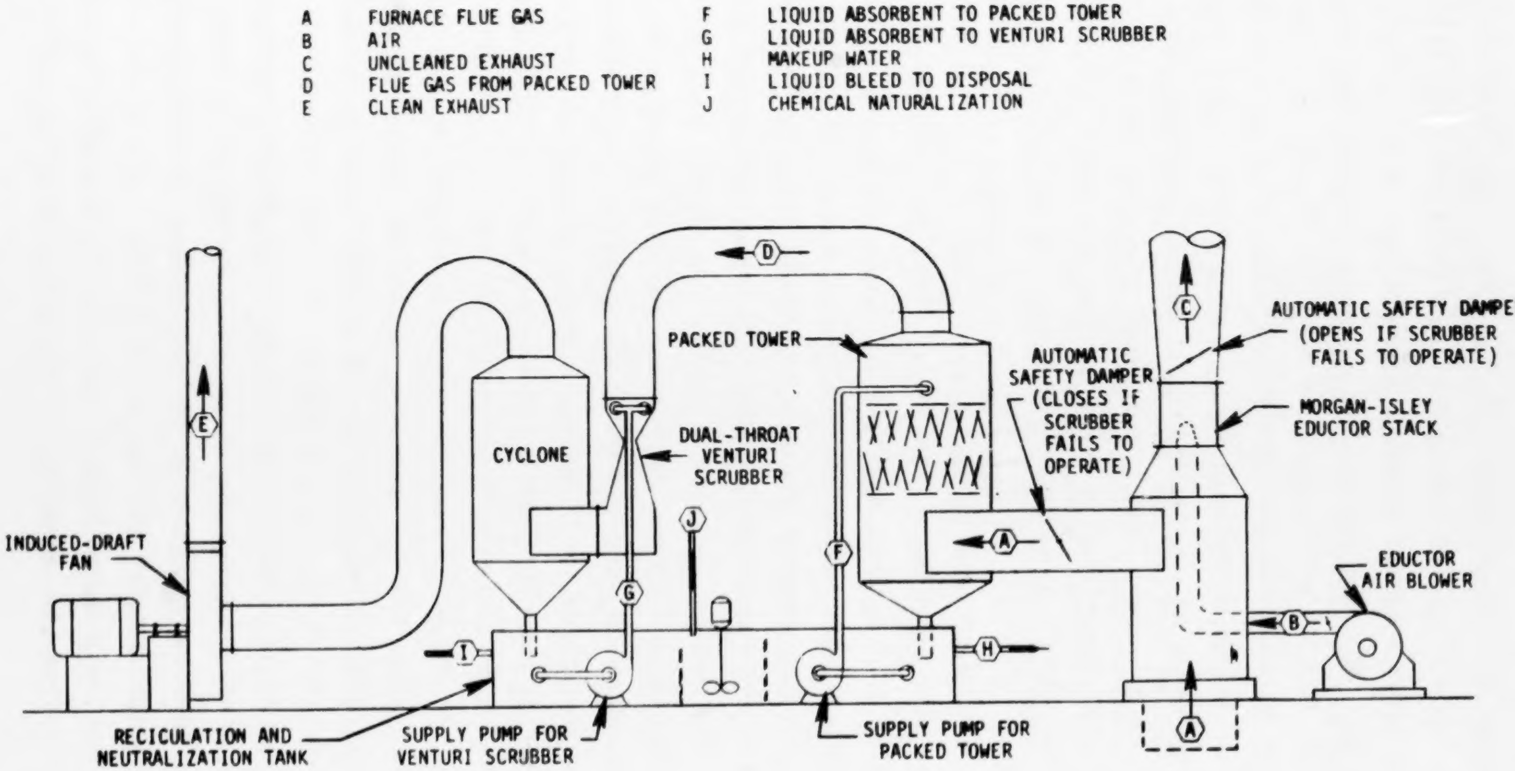
A FURNACE FLUE GAS
B AIR
C UNCLEANED EXHAUST
D FLUE GAS FROM PACKED TOWER
E CLEAN EXHAUST
F LIQUID ABSORBENT TO PACKED TOWER
G LIQUID ABSORBENT TO VENTURI SCRUBBER
H MAKEUP WATER
I LIQUID BLEED TO DISPOSAL
J CHEMICAL NATURALIZATION
D
E
C
PACKED TOWER
AUTOMATIC SAFETY DAMPER (OPENS IF SCRUBBER FAILS TO OPERATE)
AUTOMATIC SAFETY DAMPER (CLOSES IF SCRUBBER FAILS TO OPERATE)
MORGAN-ISLEY EDUCTOR STACK
CYCLONE
DUAL-THROAT VENTURI SCRUBBER
J
F
A
INDUCED-DRAFT FAN
G
EDUCTOR AIR BLOWER
B
I
H
A
RECICULATION AND NEUTRALIZATION TANK
SUPPLY PUMP FOR VENTURI SCRUBBER
SUPPLY PUMP FOR PACKED TOWER

Figure 5.8-4. Typical venturi scrubber system.[36]

TABLE 5.8-7. DEMONSTRATED SO_2 REMOVAL EFFICIENCIES OF VENTURI SCRUBBER SYSTEMS IN THE GLASS INDUSTRY[37,38]

Type of glass produced	Control system description	Fuel	Liquid-to-gas ratio, liters/standard m^3 (gal/scf)	Pressure drop, kPa (in. H_2O)	Bleed rate, liters/s (gal/min)	SO_2 removed, %	SO_2 emitted, ppm
Container glass	Full-scale system with dual-throat venturi scrubber	0.5% sulfur fuel oil	3.9 (0.0029)	8.8 (33)	Not reported	90	Not reported
Container glass	Full-scale system with packed tower and variable-throat venturi scrubber; weak alkaline solution recirculated to both	Natural gas	2.3 (0.0017)	7.5 (30)	1.1 (16.8)	75	7
Container glass	Full-scale system with packed tower and dual-throat venturi scrubber	Oil	9.4 (0.07)	8.5 (34)	0.63-9.5 (10-15)	86.5	100
Amber container glass	Pilot system with packed tower and dual-throat venturi scrubber; acidic solution used in tower; alkaline solution used in scrubber	Not reported	Not reported	6.2 (25)	0.13 (2)	91.3	10

gases.[41],[42] The spent sorbent may be landfilled or possibly recycled. In the fiberglass industry, solids produced by a sorbent system using hydrated lime (Tesisorb X) are being recycled.[42] In the container glass industry solids produced by a similar dry sorbent system have not been successfully recycled, but have been disposed of as landfill.

One patented system of dry removal (Figure 5.8-5) involves the combined use of hydrated lime and nepheline syenite for acid gas neutralization and fine particle agglomeration.[43] In this system hot furnace flue gas is first mixed with quench water, hydrated lime (Tesisorb X) for primary SO_2 removal, and secondary air to cool the gas stream to a temperature range of 94° to 427°C (200° to 800°F). Next, nepheline syenite (Tesisorb A) is added to the gas stream to capture residual SO_2 and submicrometer particulates. The gas stream enters the fabric filter where the solid product is removed for either recycling to the furnace or landfilling. Shake cycles reportedly vary from 24 to 36 hours, and pressure drops range from 1.5 to 3.0 kPa (6 to 12 in. H_2O).[42]

Table 5.8-8 summarizes SO_x emission data for dry sorbent systems at several commercial glass furnaces.[42,44] Total SO_x concentrations were reduced 80 to 95 percent at a container glass furnace, 50 to 90 percent at a fiberglass furnace, and 88 to 98 percent at a flat-glass furnace.

Mist eliminators apparently have no effect on SO_x gases. One sampling test indicated no decrease in SO_2 and SO_3 concentrations through the control device.[45]

A nucleator or double-alkali system (Figure 5.8-6) is a wet method for recovering submicrometer particulates and SO_x with relatively little energy input; the pressure drop is less than 3.7 kPa (15 in. H_2O).[43] Formation of a steam plume is avoided by use of a water recycle system with a cooling tower. As Figure 5.8-6 shows, recyclable solid product is produced. Such a system is reported in use on a fiberglass furnace and on a fluoride-opal furnace; SO_x removal efficiencies of 95 to 99 percent have been documented.[44]

Table 5.8-9 presents operating parameters for model glass plants and emission control systems, including production rate, stack height, stack diameter, stack gas exit velocity, and stack gas temperature.[46] Calculated

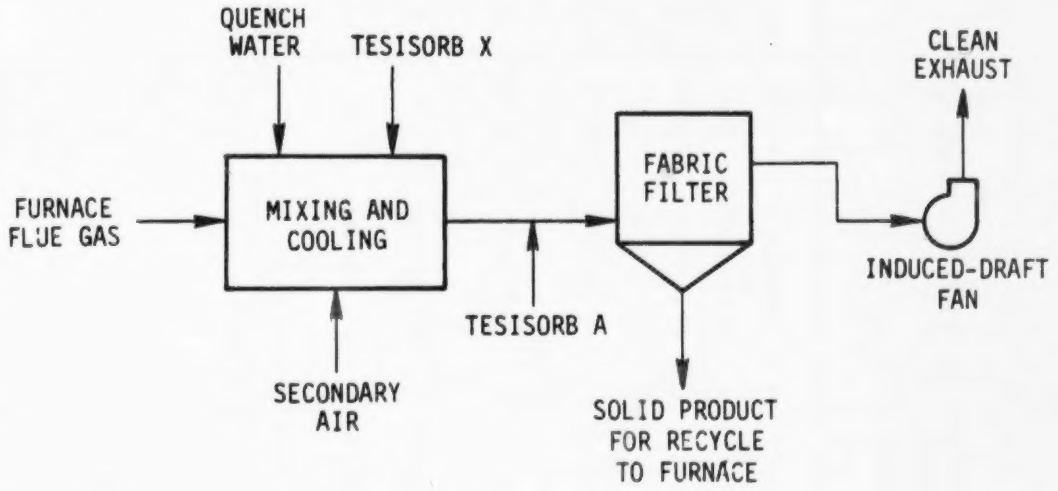
QUENCH WATER
TESISORB X
CLEAN EXHAUST
FURNACE FLUE GAS
MIXING AND COOLING
FABRIC FILTER
INDUCED-DRAFT FAN
TESISORB A
SECONDARY AIR
SOLID PRODUCT FOR RECYCLE TO FURNACE

Figure 5.8-5. Dry sorbent system.[43]

TABLE 5.8-8. EMISSION DATA FOR COMMERCIAL DRY SORBENT SYSTEMS USING TESISORB ADDITIVES[42,44]

Type of glass produced	Type of sorbent used	System capacity, standard m^3/s (scfm)	Range of shake cycle, h	Pressure drop, cm (in.) H_2O	SO_x, ppm		SO_x removal efficiency
					Inlet	Outlet	
Container	Tesisorb A plus Tesisorb X	8.0-9.0 (17,000-19,000)[a]	24-36	20-25 (8-10)	50-200	5-10	80-95
Fiberglass	Tesisorb A plus Tesisorb X	1.7 (3500)[b]	24	20-30 (8-12)	50-300	25	50-90
Fiberglass	Tesisorb A plus Tesisorb X	Not reported	24	15-30 (6-8)	130-400	24-39	80-90
Float -	Tesisorb A	0.7-0.9 (1500-2000)[c]	Not reported	Not reported	325	9-40	88-97
Float	Tesisorb A plus Tesisorb X	0.7-0.9 (1500-2000)[c]	Not reported	Not reported	325	5.5-30	91-98

[a] At 316°C (600°F).

[b] At 427°C (800°F).

[c] At 94°C (200°C).

Note: Tesisorb A is a trade name for nepheline syenide.
Tesisorb X is a trade name for hydrated lime.

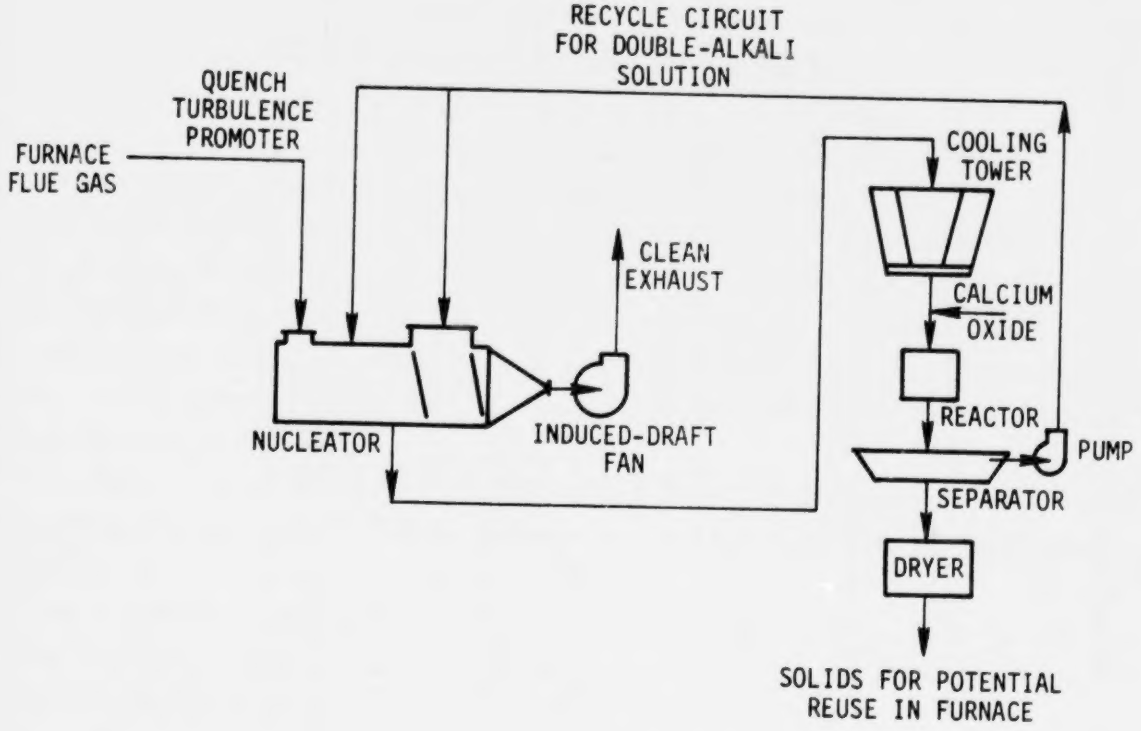
RECYCLE CIRCUIT
FOR DOUBLE-ALKALI
SOLUTION
QUENCH
TURBULENCE
PROMOTER
FURNACE
FLUE GAS
COOLING
TOWER
CLEAN
EXHAUST
CALCIUM
OXIDE
REACTOR
NUCLEATOR
INDUCED-DRAFT
FAN
PUMP
SEPARATOR
DRYER
SOLIDS FOR POTENTIAL
REUSE IN FURNACE

Figure 5.8-6. Nucleator.[43]

TABLE 5.8-9. OPERATING PARAMETERS FOR MODEL GLASS PLANTS[46]

	Container glass				Wool fiberglass		
	Uncontrolled furnace	Fabric filter controlled furnace	Scrubber controlled furnace	Electrostatic precipitator-controlled furnace	Uncontrolled furnace	Fabric filter controlled furnace	Electrostatic precipitator-controlled furnace
Production rate, Mg/day (tons/day)	227 (250)	227 (250)	227 (250)	227 (250)	181.6 (200)	181.6 (200)	181.6 (200)
Stack height, m (ft)	21.3 (70)	25.9 (85)	18.3 (60)	18.3 (60)	27.4 (90)	25.9 (85)	18.3 (60)
Stack diameter, m (ft)	2.29 (7.5)	2.07 (6.8)	1.74 (5.7)	2.29 (7.5)	1.89 (6.2)	1.71 (5.6)	1.89 (6.2)
Stack exit velocity, m/s (ft/s)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)
Stack flow rate, m^3/s (acfm)	37.76 (80,000)	30.68 (65,000)	21.80 (46,200)	37.61 (79,700)	25.86 (54,800)	21.05 (44,600)	25.86 (54,800)
Stack temperature, °K (°F)	590 (603)	480 (405)	340 (153)	590 (603)	590 (603)	480 (405)	590 (603)

	Pressed and blown, 45 Mg/day (50 tons/day)			Pressed and blown, 91 Mg/day (100 tons/day)			Flat	
	Uncontrolled furnace	Fabric filter controlled furnace	Electrostatic precipitator-controlled furnace	Uncontrolled furnace	Fabric filter controlled furnace	Electrostatic precipitator-controlled furnace	Uncontrolled furnace	Electrostatic precipitator-controlled furnace
Production rate, Mg/day (tons/day)	45.4 (50)	45.4 (50)	45.4 (50)	90.8 (100)	90.8 (100)	90.8 (100)	635.6 (700)	635.6 (700)
Stack height, m (ft)	27.4 (90)	25.9 (85)	18.3 (60)	27.4 (90)	25.9 (85)	18.3 (60)	21.3 (70)	18.3 (60)
Stack diameter, m (ft)	1.02 (3.36)	1.02 (3.36)	1.14 (3.73)	1.45 (4.76)	1.45 (4.76)	1.61 (5.27)	4.39 (14.4)	4.39 (14.4)
Stack exit velocity, m/s (tons/day)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)	9.14 (30)
Stack flow rate, m^3/s (acfm)	7.55 (16,000)	7.55 (16,000)	9.30 (19,700)	15.10 (32,000)	15.10 (32,000)	18.55 (39,300)	138.28 (293,000)	138.28 (293,000)
Stack temperature, °K (°F)	480 (405)	480 (405)	590 (603)	480 (405)	480 (405)	590 (603)	480 (405)	480 (405)

exhaust gas velocities are based on an assumed 10.5 percent oxygen concentration in the furnace exhaust, which is equivalent to 100 percent excess oxygen. Stack diameters are calculated to maintain a stack gas exit velocity of 9 m/s (30 ft/s).

5.8.2.2 Control Cost--

Information on the costs of SO_x pollution control in the glass industry is limited. Figure 5.8-7 presents reported and estimated capital costs for the installation of scrubber control systems on glass furnaces.[47] The reported costs are for scrubbers designed primarily for control of particulate matter. Values are in January 1978 dollars. Although the data do not permit a reliable comparison between the estimated and reported costs, the location of the points suggests relatively good agreement.

Table 5.8-10 summarizes other reported cost data and performance parameters for control systems applied to glass manufacturing furnaces.[48] Although these systems are designed primarily for particulate control, they also achieve various levels of secondary SO_x control, as noted in the table. All costs have been adjusted to July 1979 dollars by using the Chemical Engineering Cost Index.

Data on the cost of electric melting appear contradictory. One report indicates that electric melting is several times more costly than conventional pollution control devices for reducing air emissions.[48] Another source presents investment and operating costs for various melting process and pollution control systems and suggests that the overall cost of electric melting compares well with the cost of firing natural gas or oil.[49]

5.8.2.3 Energy and Environmental Impact--

In 1971 a total of 264 PJ (250 trillion Btu) was consumed by the glass industry.[50] This energy came from the following sources: 1.6 percent from coal, 4.5 percent from fuel oil, 5.2 percent from electricity, and 88.7 percent from natural gas.[51] Coal is not a furnace fuel, but can be used as a batch ingredient or as a plant boiler fuel. Data for 1976 show a trend toward increased use of fuel oil and electricity. Fuel oil provided 14 percent of the energy consumed by the glass industry in 1976, electricity provided 11 percent, and natural gas supplied 74 percent.[52] Although,

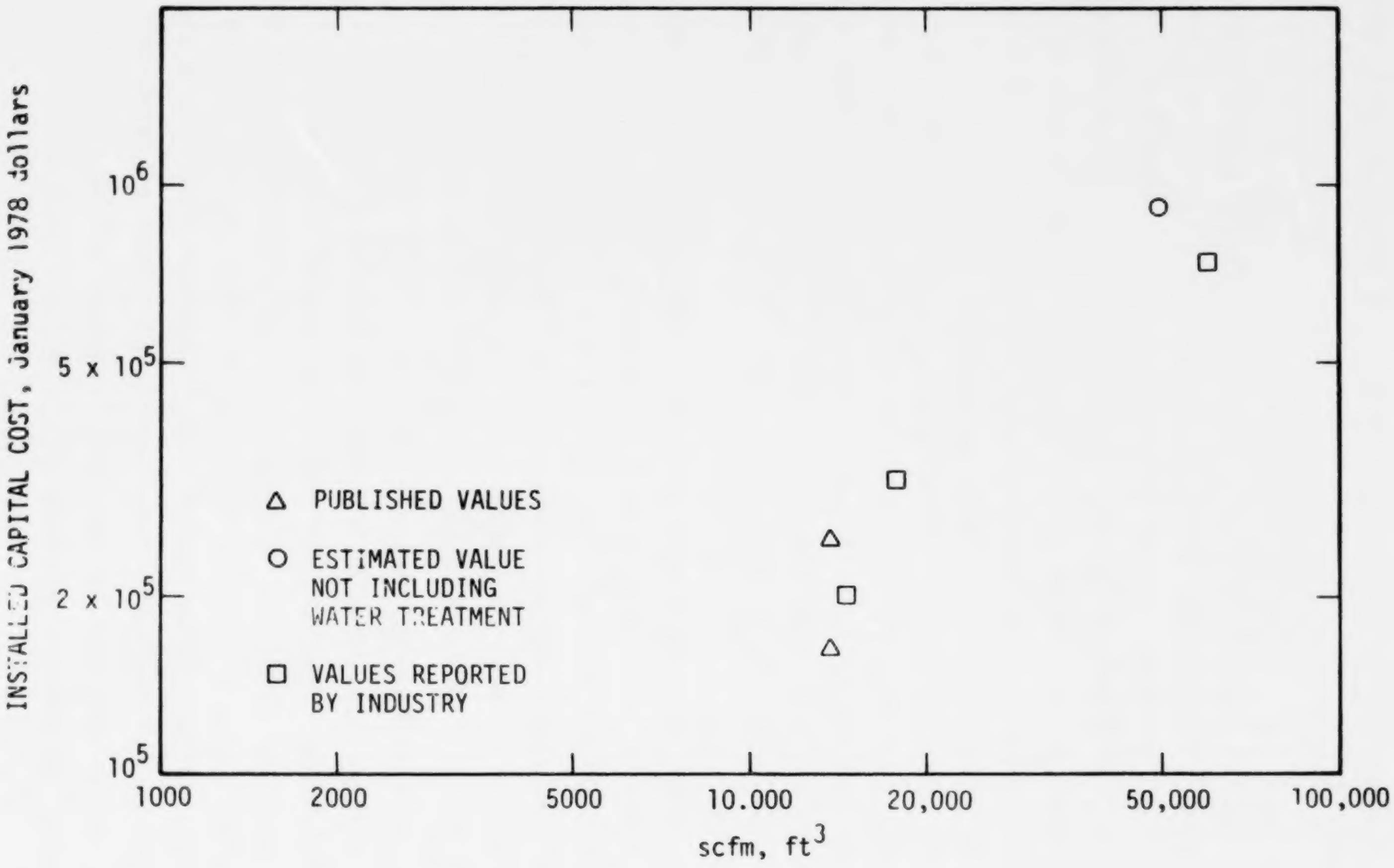

Figure 5.8-7. Reported and estimated installed costs of scrubber control systems on glass furnaces.[47]

TABLE 5.8-10. PERFORMANCE AND COST DATA FOR EMISSION CONTROL SYSTEMS AT A GLASS FURNACE PRODUCING 1.57 kg/s (150 tons/day)[48]

	Dry sorbent systems	Venturi scrubber system	Nucleator
SO_x removal, %	25-95 (all sorbents) 90-96 (Tesisorb A+X)	90-98[a]	95-99
Opacity, %	0	<10	<10
Solids production, kg/h (lb/h)	59-60 (131-132)	38 (84)	37 (82)
Installed capacity, watts (horsepower)	44,742	186,425 (250)	119,312 (160)
Installed capital cost, $[b]	520,000[c]	715,000	715,000
Cost of emission control, $/Mg ($/ton)b			
Utilities[d]	0.20 (0.18)	0.81 (0.74)	0.62 (0.56)
Amortization[e]	1.06 (0.96)	1.46 (1.33)	1.46 (1.33)
Maintenance[f]	0.37 (0.34)	0.80 (0.73)	0.89 (0.81)
Chemicals[g]	0.20 (0.18)	0.33 (0.30)	0.15 (0.14)
Additional operating labor[h]	0.20 (0.18)	0.40 (0.36)	0.40 (0.36)
Solids reuse or disposal[i]	0.08 (0.07)	0.04 (0.04)	0.04 (0.04)
Total additional cost over fossil fuel	2.00-2.11 (1.81-1.91)	3.84 (3.50)	3.56 (3.24)
Credit for recoverable chemicals[j]	0.09-0.22 (0.08-0.20)	0.22 (0.20)	0.22 (0.20)
Net cost	1.89-1.91 (1.71-1.73)	3.62 (3.30)	3.34 (3.04)

[a] This value may be high; SO_x efficiencies reported elsewhere for venturi scrubber systems range from 75 to 90 percent.

[b] All costs adjusted to July 1979 based on 237 as Chemical Engineering Cost Index value; 100 is the value for 1957-59.

[c] In multiple furnace installations.

[d] Utilities:
fossil fuel, $1.30/10^9 J ($1.37/10^6 Btu)
electricity, $0.03/kWh;
steam, $1.72/Mg ($0.78/1000 lb).

[e] Amortization: 10-year straight line.

[f] Maintenance:
dry sorbent, 3%
wet systems, 6%.

[g] Chemicals:
NaOH, $143/Mg ($130/ton);
$Ca(OH)_2$, $36/Mg ($33/ton);
Tesisorb A, $72/Mg ($65/ton);
Tesisorb X, $40/Mg ($36/ton).

[h] Labor: $19,500/man-year

[i] Solids reuse or disposal: $8/Mg ($7/ton).

[j] Recovery value: $29/Mg ($26/ton).

theoretically, coal could be used as an energy source, its use appears impractical because of problems associated with poor glass quality, refractory damage, and diminished furnace life.[53]

Natural gas has continued to be the preferred fuel because it burns clean, does not affect glass characteristics, and allows for longer furnace life than other fuels. Nevertheless, because of rising prices and allocation problems, some natural-gas-fired units have been replaced by oil-fired ones. Consumption of electricity is also expected to continue to increase, especially in the flat glass segment.[54] Preliminary studies on preheating the melt indicate that a 50 percent process energy savings is possible, as well as reductions in pollutant emissions.[55]

The energy required to manufacture glass varies considerably according to the glass type. Glass manufacturers indicate that fossil-fuel-fired melting operations require 4.2 to 7.4 GJ (4 to 7 million Btu) to produce 0.907 Mg (1 ton) of container glass, 6.3 to 12.7 GJ (6 to 12 million Btu) to produce 0.907 Mg (1 ton) of flat glass, and 6.3 to 42 GJ (6 to 40 million Btu) to produce 0.907 Mg (1 ton) of pressed and blown glass.[56]

Estimates of energy costs for air pollution control range from 0.1 to 15 percent of the energy consumed by the industry.[57,58] These energy costs are indirectly related to SO_x control because SO_x emissions are only controlled by the industry to the extent that SO_x is removed with particulates or to the extent that low-sulfur fuels are used.

The environmental effects of a dry sorbent system are minimal because it creates no wastewater discharge and because the solids produced may be recycled or safely landfilled.[59] A venturi scrubber system typically incorporates a recycle system with an alkaline injection to control pH and a bleed stream of about 0.13 liter/s (2 gal/min) on a furnace producing 2.1 kg/s (200 tons/day) of soda-lime glasses.[60] The concentration of sodium sulfate in this wastewater stream is 3 to 4 percent. Although discharges of this nature from individual venturi systems may have significant local environmental impact and require treatment, the total impact on water pollution from the glass industry is considered negligible because of the limited number of glass facilities that are expected to utilize this system.[61]

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5.9 MINERAL PRODUCTS

The three major mineral products industries that generate SO_2 emissions are the portland cement, lime, and clay and brick manufacturing industries. The primary source of SO_2 emissions in each of these industries is combustion of fuel used in kilns and drying operations. The fuels are natural gas, oil, coal, and wood.

5.9.1 Process Descriptions and Emission Sources

5.9.1.1 Lime Production--

The manufacture of lime (quicklime) involves the calcining of limestone (CaCO or $CaCO_3 \cdot MgCO_3$) to release carbon dioxide and form quicklime (CaO or $CaO \cdot MgO$). Calcitic limestone is approximately 95 percent calcium carbonate. Dolomitic limestone contains 30 to 40 percent magnesium carbonate, and the remainder is calcium carbonate. Quicklime may be further processed to yield dolomitic pressure-hydrated lime, high-calcium lime, or dolomitic hydrated lime, depending on the limestone used.[1]

As illustrated in Figure 5.9-1,[2] lime production operations include limestone quarrying, crushing and sizing, calcining, hydrating, milling, sizing by screening and air separation, storage, packaging, and shipping.

Calcining in the U.S. plants is performed either in stationary vertical kilns of various designs or in horizontal rotary kilns. The oldest type of continuous kiln is the vertical or shaft kiln, which is most efficient in terms of fuel economy but is limited in capacity per individual unit. Horizontal rotary kilns are used to produce slightly more than 90 percent of the total lime production in the United States.[3] Even though fuel economy is lower and capital investment is greater for rotary kilns, the trend is toward use of these types because of their high capacity per unit.

Rotary kilns and vertical kilns may be fired with natural gas, fuel oil, or coal (pulverized coal for rotary kilns). Because of the uncertainty of natural gas availability and rising energy costs, the trend has been toward coal firing; coal is now used to produce more than 60 percent of the commercial lime manufactured in this country.[4]

The following discussion concerns sulfur dioxide (SO_2) emissions from rotary lime kilns (the only source of SO_2 emissions at the plant), because

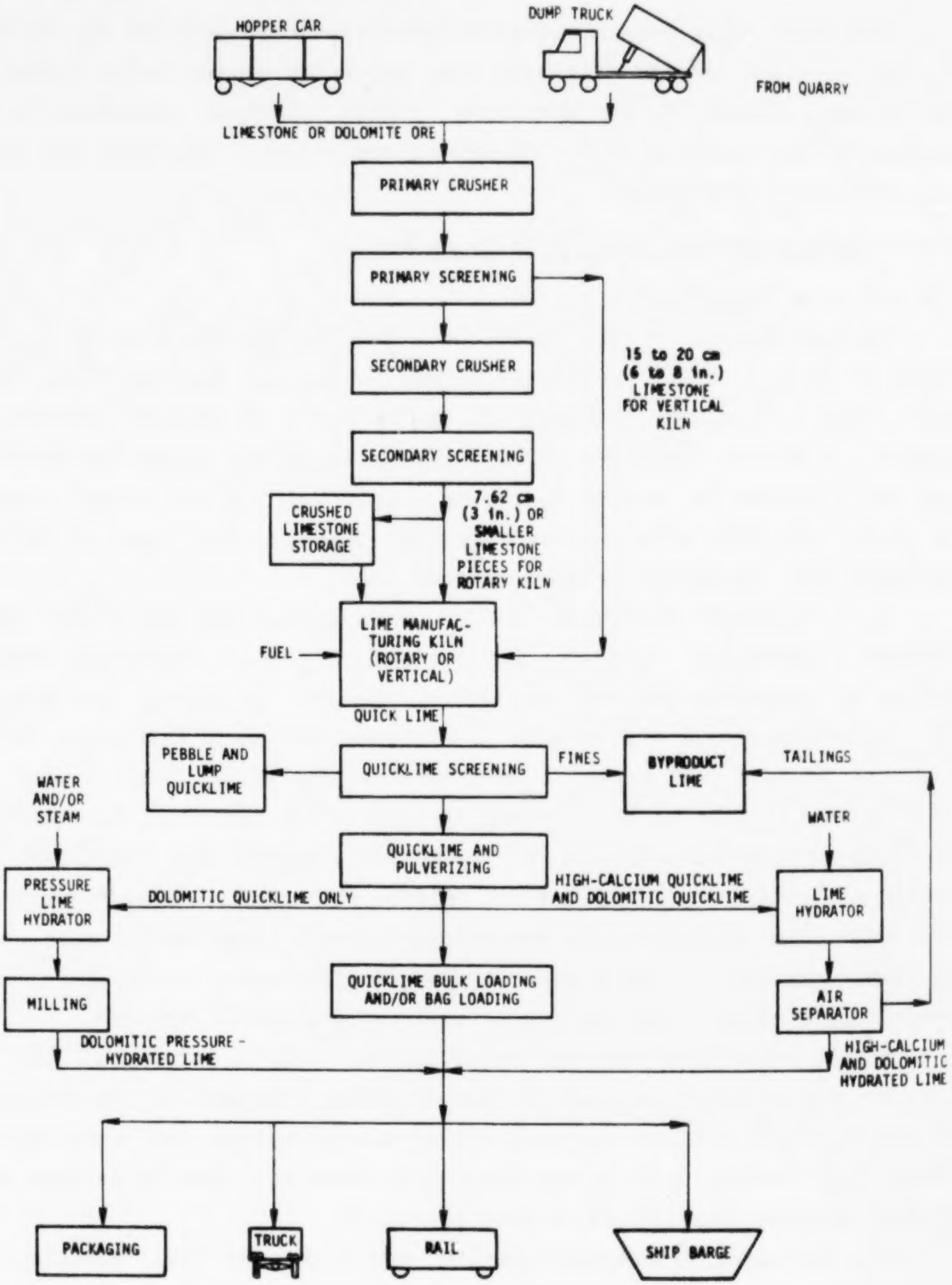
HOPPER CAR
DUMP TRUCK
FROM QUARRY
LIMESTONE OR DOLOMITE ORE
PRIMARY CRUSHER
PRIMARY SCREENING
15 to 20 cm (6 to 8 in.) LIMESTONE FOR VERTICAL KILN
SECONDARY CRUSHER
SECONDARY SCREENING
CRUSHED LIMESTONE STORAGE
7.62 cm (3 in.) OR SMALLER LIMESTONE PIECES FOR ROTARY KILN
FUEL
LIME MANUFACTURING KILN (ROTARY OR VERTICAL)
QUICK LIME
PEBBLE AND LUMP QUICKLIME
QUICKLIME SCREENING
FINES
BYPRODUCT LIME
TAILINGS
WATER AND/OR STEAM
QUICKLIME AND PULVERIZING
WATER
PRESSURE LIME HYDRATOR
DOLOMITIC QUICKLIME ONLY
HIGH-CALCIUM QUICKLIME AND DOLOMITIC QUICKLIME
LIME HYDRATOR
MILLING
QUICKLIME BULK LOADING AND/OR BAG LOADING
AIR SEPARATOR
DOLOMITIC PRESSURE-HYDRATED LIME
HIGH-CALCIUM AND DOLOMITIC HYDRATED LIME
PACKAGING
TRUCK
RAIL
SHIP BARGE

Figure 5.9-1. Process flow diagram for lime production.[2]

virtually all of the new kilns installed in the past 10 years have been rotary kilns. Because of limited availability and high costs of oil and natural gas, most installations will be rotary lime kilns designed to burn coal.

Sulfur is present in most limestone and in all fuels used in the industry, except natural gas. The sulfur in the limestone does not normally contribute a substantial portion of the total SO_2 emissions from a rotary kiln. The major source of SO_2 is the sulfur in the fuel.

During fuel combustion, most of the sulfur in the fuel is converted to SO_2. Some of the SO_2 reacts with the lime product or with the lime dust, and some is emitted with the kiln off-gas. The amount of SO_2 that reacts with the lime product or lime dust depends on the chemical composition of the stone, the temperature in the kiln, the amount of excess oxygen in the kiln, and the amount and particle size of the lime dust inside the kiln.[5] Table 5.9-1 presents parameters required to perform dispersion calculations on two model lime kiln plants. When coal or oil with a sulfur content of less than 1.0 percent is fired, only about 10 percent of the sulfur in the fuel is vented to the atmosphere as SO_2. When fuels with higher sulfur content are used, the SO_2 removal efficiency of the lime may be reduced to about 50 percent.[6,7]

TABLE 5.9-1. LIME KILN MODELING PARAMETERS

Type of collector	Stack gas temperature	Stack diameter	Stack gas velocity
Dry	188°C (370°F)	0.94 m (3 ft)	5.79 m/s (19 ft/s)
Wet	66°C (150°F)	0.88 m (2.9 ft)	5.99 m/s (19.7 ft/s)

5.9.1.2 Portland Cement Manufacture--

The cement industry includes all establishments engaged in the manufacture of hydraulic cement (generic name: portland cement) and of masonry, natural, or pozzolana cements. This description is limited to the production of portland cement because it accounts for 95 percent of the total cement manufactured in the United States.

Cement is produced by heating to the point of fusion a finely ground combination of limestone, cement rock, marl, or oyster shells with shale, clay, sand, iron ore, or aluminum. The fused product, called cement clinker, is ground to a fine powder and shipped in bags or by bulk carrier.

Figure 5.9-2 illustrates the process flow of a typical cement plant. Initially, the raw materials (limestone, cement, rock, marl, or oyster shells) are combined with shale, clay, sand, iron ore, or aluminum and with other trace materials and ground to the desired gradation. Either the dry process or the wet process is used. In the dry process, heat for drying is provided by direct dryer firing or hot kiln exhaust gases. The finished finely ground raw material is then conveyed to the blending operation and later fed to the kiln. In the wet process, individual raw material slurries may be blended after grinding. The finished slurry used as a kiln feed may be 30 to 40 percent water or it may be dewatered to approximately 20 percent water and fed as a filter cake. The mixed materials are heated in a rotary kiln and transformed into clinker at approximately 1595°C (2889°F).[8] The clinker is discharged from the kiln, cooled, ground to the desired fineness, and combined with gypsum to control the setting time of the concrete. The finished cement product is then stored for later packaging and shipment.[9]

Emissions also include the products of combustion of the fuel used in the rotary kilns and drying operations; these emissions are typically NO_x and small amounts of SO_2.[9]

The limited available data on SO_2 emissions from uncontrolled kilns using both wet and dry processes indicate a factor of 5.1 kg/Mg (10.2 lb/ton) attributable to the mineral content of the raw materials and factors of 2.1S and 3.4S with combustion of oil and of coal (where S is the percent sulfur content of the fuel in percent).[10] Emissions of SO_2 attributable to firing of gas are negligible. These factors take into account the reactions with alkaline dusts when no fabric filters are used. With fabric filters, about 50 percent more SO_2 is removed in reactions with the alkaline filter cake.[11] The 5.1-kg/Mg value accounts for part of the available sulfur remaining in the product because of its alkaline nature and affinity for SO_2. Total emissions from the kiln are the sum of the mineral content factor and the fuel sulfur factor.

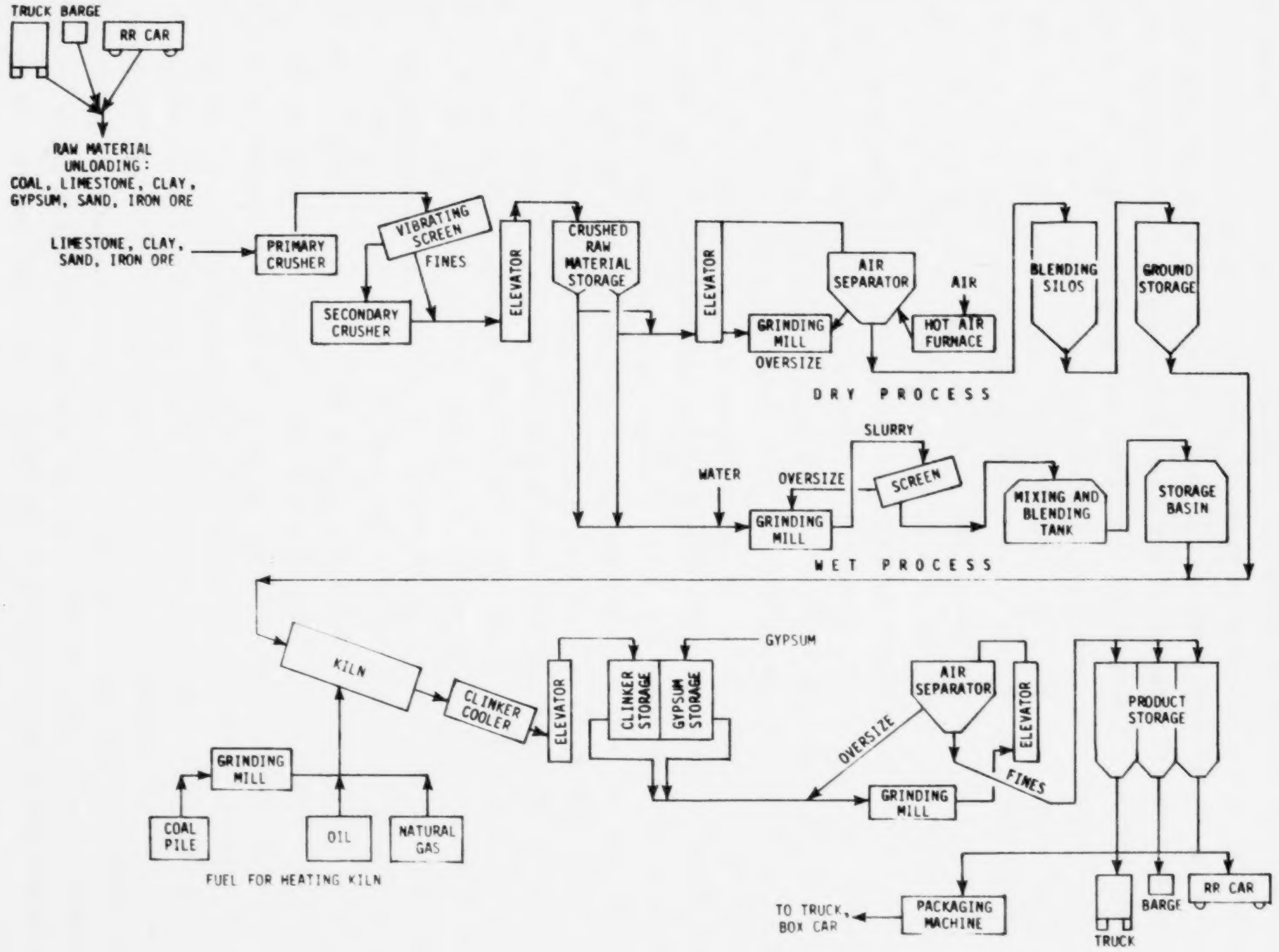
TRUCK BARGE
RR CAR
RAW MATERIAL UNLOADING: COAL, LIMESTONE, CLAY, GYPSUM, SAND, IRON ORE
LIMESTONE, CLAY, SAND, IRON ORE
PRIMARY CRUSHER
VIBRATING SCREEN
FINES
SECONDARY CRUSHER
ELEVATOR
CRUSHED RAW MATERIAL STORAGE
ELEVATOR
GRINDING MILL
OVERSIZE
AIR SEPARATOR
AIR
HOT AIR FURNACE
BLENDING SILOS
GROUND STORAGE
DRY PROCESS
WATER
OVERSIZE
SLURRY
SCREEN
GRINDING MILL
MIXING AND BLENDING TANK
STORAGE BASIN
WET PROCESS
KILN
CLINKER COOLER
ELEVATOR
GYPSUM
CLINKER STORAGE
GYPSUM STORAGE
AIR SEPARATOR
ELEVATOR
OVERSIZE
FINES
GRINDING MILL
PRODUCT STORAGE
GRINDING MILL
COAL PILE
OIL
NATURAL GAS
FUEL FOR HEATING KILN
TO TRUCK, BOX CAR
PACKAGING MACHINE
TRUCK
BARGE
RR CAR

Figure 5.9-2. Process flow diagram for cement manufacturing.

5.9.1.3 Clay and Brick Production--

The clay and brick production industry consists of those companies involved in mining and beneficiating of clay minerals and subsequent processing of these clay minerals to make bricks. The clay minerals vary widely in chemical composition and physical properties, but are basically natural, earthy, fine-grained, hydrated aluminum silicates, which are plastic when wet, rigid when dry, and vitreous when fired. The U.S. Bureau of Mines classifies the clay industry into six categories: ball clay, bentonite, fire clay, fuller's earth, kaolin, and common clay plus shale.[12]

Figure 5.9-3 is a process flow sheet for the clay and brick manufacturing industry. The clay ore is excavated from open pit mines, then crushed in jaw or gyratory crushers or hammer mills (primary crushing); secondary crushing is done if needed. The material is then screened, dried from 20 to 30 percent moisture to 1 to 15 percent moisture content in rotary dryers, and optionally dry-ground in ball, rod, or roller mills. Crushed common clay or beneficiated clay is cut, formed, and molded in the extruding process; it is then dried and finally fired in continuous tunnel kilns.[13] Batch-type periodic kilns are also sometimes used to fire clay and brick, but they are not widely used especially in modern plants. Periodic kilns require two to three times more fuel as compared with a tunnel kiln.[14]

The kiln may be fired with natural gas, oil, coal, or wood. The current trend is toward coal and wood. Waste heat from the cooling section of the kiln is generally used to dry the bricks before they enter the kiln. Makeup heat for the dryers, if necessary, is supplied by combustion of the same fuels used for firing the kiln.[15]

Table 5.9-2 presents emission factors for SO_2 emitted from the combustion of natural gas, fuel oil, and coal in the firing operation of periodic and tunnel kilns without control systems.[16-18] Based on these erosion factors, from a 90.7-Mg/day (100-tons/day) kiln firing 6.8 Mg/day (7.5 tons/day) coal, gases are discharged to the atmosphere at an estimated rate of 7.08 m^3/s (15,000 ft^3/min) and a temperature of 132°C (270°F); these gases contain 36 kg/h (80 lb/h) SO_2.[15] It is not known what portion of the SO_2 reacts with the clay of the bricks or what portion of the sulfur in the clay is emitted as SO_2; however, it is likely that these amounts are minimal.

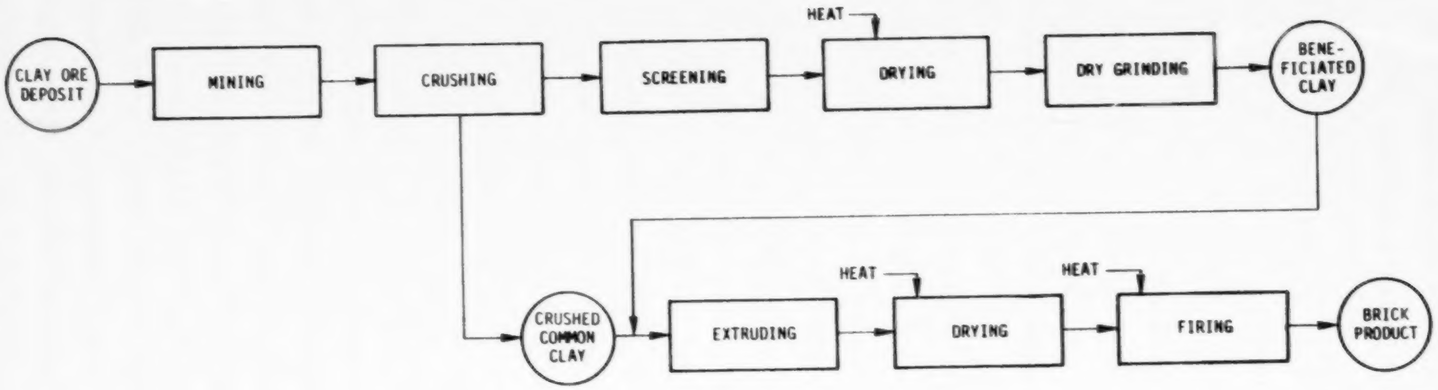
CLAY ORE DEPOSIT
MINING
CRUSHING
SCREENING
HEAT
DRYING
DRY GRINDING
BENE-FICIATED CLAY
CRUSHED COMMON CLAY
EXTRUDING
HEAT
DRYING
HEAT
FIRING
BRICK PRODUCT

Figure 5.9-3. Process flow diagram for clay and brick production.

TABLE 5.9-2. SO_x EMISSION FACTORS FOR BRICK MANUFACTURING WITHOUT CONTROLS[16-18]

	kg SO_x/Mg brick	(lb SO_x/ton brick)
Tunnel kilns		
Gas-fired	a	(a)
Oil-fired	2.0S[b]	(4.0S)
Coal-fired	3.6S	(7.2S)
Periodic kilns		
Gas-fired	a	(a)
Oil-fired	2.95S	(5.9S)
Coal-fired	6.0S	(12.0S)

[a] Negligible.

[b] "S" denotes the percent of sulfur in the fuel.

5.9.2 Control Techniques

5.9.2.1 Description--

The primary means of reducing SO_2 emissions from the lime, cement, and clay and brick manufacturing industries are the utilization of low-sulfur fuels and/or the application of some type of emission control device. Clean fuels, as a means of attaining desired SO_2 emissions, may not be available as a viable option in the future because of increasing use of coal and reduced supplies of cleaner fuels. The sulfur content of coal is typically higher than that of natural gas and oil, which results in increased SO_2 emissions. The SO_2 emissions from the mineral products industries are 0.22 percent (600,000 Mg/yr, 660,000 tons/yr) of the nationwide SO_2 emissions.[19]

Lime--The fabric filter and electrostatic precipitator (ESP), which are the control devices used predominantly for control of particulate matter from lime kilns, also provide SO_2 control by increasing the time available for the reaction of SO_2 with the lime. Wet scrubbers are generally more efficient for SO_2 control than ESP's or fabric filters. In tests of a rotary lime kiln firing 2.96 percent sulfur coal, SO_2 emissions were measured at the inlet and outlet of a wet scrubber with a pressure drop of 5.5 kPa (22 in. H_2O); emissions were 3.8 kg of SO_2 per megagram of limestone (7.6 lb/ton) uncontrolled, and the estimated control efficiency (from reaction with lime in the kiln) was about 50 percent, based on the sulfur content of the coal. The wet scrubber alone provided a control efficiency of

96 percent, yielding an overall control efficiency of 98 percent, again based on the sulfur content of the coal.[6] A similar test on a lime kiln firing 2.97 percent sulfur coal and controlled by a fabric filter indicated an overall SO_2 control efficiency of 82 percent. Another similar test on a lime kiln burning 1.05 percent sulfur fuel oil and controlled by an ESP indicated an overall SO_2 removal efficiency of 88 percent.[6]

Cement--Most of the SO_2 emissions are inherently controlled in the process of cement manufacturing because about 75 percent of the raw feed is converted to calcium oxide, which reacts with SO_2. In addition, the presence of sodium and potassium compounds in the raw material aids in the direct absorption of SO_2 into the product. The variable chemistry and operating conditions in U.S. cement plants affect the amount of SO_2 removal and, in some cases, the quality of the product. Sulfur dioxide removal of this type is 75 percent in plants for which data are available. Sulfur dioxide also is removed by this same mechanism by fabric filters, in which the SO_2-laden gas contacts the collected cement dust. The degree of control by SO_2 absorption depends upon the alkali and sulfur contents of the raw materials and fuel.[20] Limited information is available concerning specific SO_2 control systems for these sources.[21]

Brick--No specific information is available on SO_2 control systems for the dryers and kilns of brick and clay production industries.[21]

5.9.2.2 Control Cost--

The cost of burning low-sulfur fuels would be determined by the difference between the cost of the standard fuel burned and that of the low-sulfur fuel, which usually is higher.

Little information is available on the cost of SO_2 scrubbers applicable to these industries. Investment capital costs of wet scrubbers for lime kilns range from $311,000 for a scrubber with a pressure drop of 2.24 kPa (9 in. H_2O) on a 114-Mg/day (125-ton/day) kiln to $793,000 for a scrubber with a pressure drop of 5.5 kPa (22 in. H_2O) on a 454-Mg/day (500-ton/day) kiln; total annualized costs of these units are $137,000 and $537,000, respectively.[22] These costs are for scrubbers designed primarily for particulate control. The operating costs of scrubbers on lime kilns are more than twice the costs of dry control systems such as ESP's and fabric filters.[23]

5.9.2.3 Energy and Environmental Impacts--

Section 3.2.1.3 discusses the energy and environmental impacts from SO_2 control by fuel switching. Scrubbers typically use considerably more energy than dry collectors, which are the control devices used predominantly in these industries. In the lime industry, a scrubber with a pressure drop of 5.5 kPa (22 in. H_2O) needs six times more energy to operate than a baghouse, which is equivalent to a total plant energy increase of 4 percent. If this energy is produced in a coal-fired power plant, an additional 21 Mg (23 tons) of SO_2 per year would be produced, assuming that the power plant conforms to the standard of performance of 520 ng/J (1.2 lb of SO_2/million Btu) heat input.[24]

The temperature of the stack gas following a scrubber is lower than that following a fabric filter or ESP. Consequently, the dispersion characteristics of the emissions are not as favorable. Because the scrubber gases at lower temperatures are less buoyant, the maximum predicted concentration of SO_2 in the ambient air is only slightly lower from the scrubber. If the possibility of aerodynamic downwash is neglected, no difference is predicted in the maximum ambient concentrations resulting from scrubbers and dry collectors.[25]

Because they produce a sludge that necessitates solid waste management and water pollution control, scrubbers might pose important problems where effluent guidelines require zero discharge.

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5.10 EXPLOSIVES MANUFACTURE

An explosive is a material that decomposes rapidly and spontaneously under the influence of thermal or mechanical shock, with the evolution of large quantities of heat and gas. Primary characteristics by which explosives are classified are brisance (shattering power) and sensitivity to explosion initiation. Other properties, such as heat and production of toxic gas, may be important in the selection of explosives for specific uses (e.g., underground mining operations).

Explosives are classified as either high or low explosives, and as primary or secondary. Primary high explosives are not only very powerful but also are very sensitive to thermal or mechanical shock. Because of these properties they are used only in small quantities as initiating explosives or detonators to set off larger quantities of other explosives.

Secondary high explosives are less sensitive to mechanical or thermal shock, but explode with great violence when set off by an initiating explosive. Examples are ammonium nitrate mixtures, nitroglycerine (NG), and 2,4,6-trinitrotoluene (TNT).

The low explosives undergo relatively slow autocombustion when set off, and evolve large volumes of gas in a definite and controllable manner. Nitrocellulose (NC) is a common example. Black powder was once a principal low explosive, but industrial use has not been reported since 1971.

The explosives manufacturing industry consists of a commercial and a military sector. Ammonium nitrate mixtures are the explosives most widely produced and used by the commercial sector because ammonium nitrate is inexpensive and readily available. Ammonium nitrate is used in over 90 percent of all commercially manufactured explosives.

Other commercially produced explosives include NG (in bulk and in dynamite forms), nitrostarch, RDX, and PETN. Apparent annual consumption of commercial explosives and blasting agents in the United States in 1977 increased 11.4 percent above the 1976 level to 1.68 Tg (3.7 billion lb).[1]

The military sector of the explosives industry produces large quantities of NG (~0.68 Gg, 1.5 million lb), NC (~13.6 Gg, 30 million lb), and TNT (not produced in the private sector).[2] The current major U.S. military explosive, Compound B, is a blend of 40 percent TNT and 60 percent RDX. The current peacetime production of military explosives is very slow, and active production sites are few.

Most explosives currently produced are nitrogen-based organic compounds. From a process viewpoint, the nitrogen-based explosives of major concern with respect to SO_x emissions are TNT, NC, and NG.

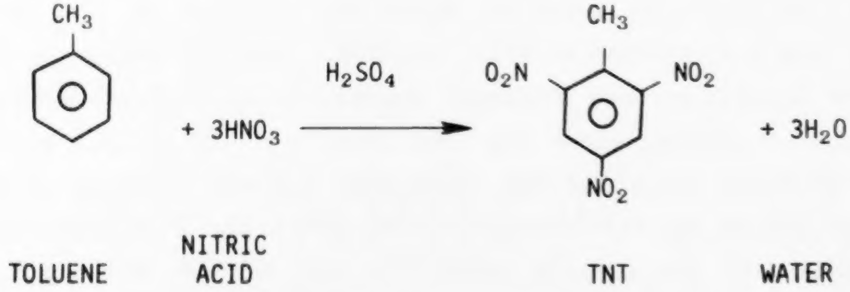
5.10.1 Process Description and SO_x Emission Sources

Manufacture of TNT, NC, and NG generally follows the flow scheme shown in Figure 5.10-1.[3] Concentrated acids are reacted with an organic material in a nitration step. One of the acids is a nitrating acid (HNO_3), and the other is a reaction catalyst, sulfuric acid (H_2SO_4). The explosive product is separated from the acid phase, washed, purified, and dried. The acid phase is recovered, reconcentrated, and recycled. Acid fume recovery may be economically advantageous in larger processes.

Emission sources can be classified as either vents from nitration vessels, washing units, and acid storage tanks, or tail gases from absorption towers on acid production, recovery, or concentration units. In addition to nitrogen oxides, major pollutants from this industry are SO_2 and sulfuric acid mist.

5.10.1.1 TNT--

TNT may be prepared by either a batch, three-stage nitration process or a continuous process known as the Canadian Industries Limited process. In either case, toluene and nitric acid are the raw materials, and oleum (fuming sulfuric acid) is used as a reaction catalyst. The overall reaction may be expressed as:



In the batch process a special mixture of nitric acid and oleum is fed to each of the three reactors containing the toluene-nitrobody mixture to

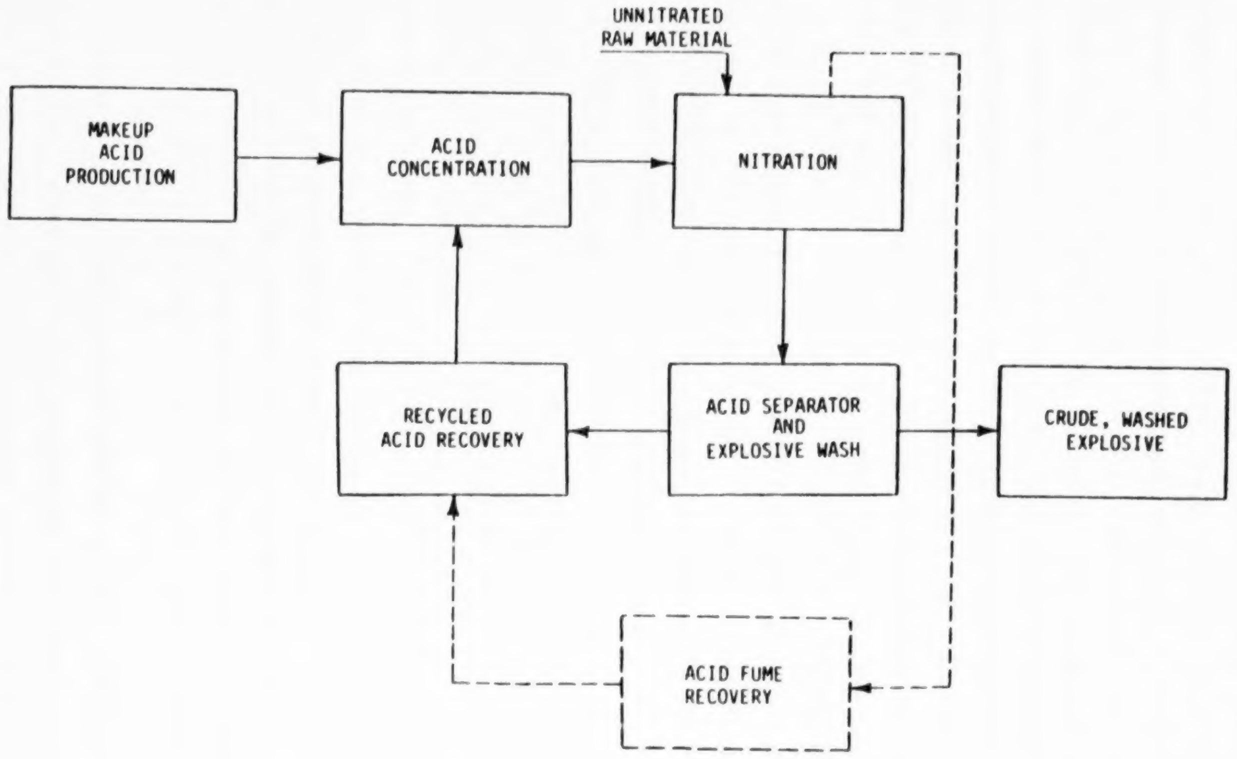

UNNITRATED RAW MATERIAL
MAKEUP ACID PRODUCTION
ACID CONCENTRATION
NITRATION
RECYCLED ACID RECOVERY
ACID SEPARATOR AND EXPLOSIVE WASH
CRUDE, WASHED EXPLOSIVE
ACID FUME RECOVERY

Figure 5.10-1. Generalized explosive manufacturing process.[3]

produce first mono-, then di-, and finally trinitrotoluene or TNT. Sulfuric acid is recovered from the spent acids in the primary nitrator by first separating it from the nitric acid and then boiling it in a drum concentrator to remove excess water.

The product from the third nitration vessel is sent to a wash house, where it is water-washed to remove excess acids. The purification wastewater, known as "red water," is either concentrated and sold to the paper industry, incinerated, or discharged directly as a liquid waste stream.

In the continuous process, the nitration of toluene is accomplished by moving the toluene-nitrobody mixture countercurrent to the oleum-nitric acid mixture. The spent acid mixture from the TNT nitrators is heated to boil off the nitric acid, leaving in the tower bottoms dilute sulfuric acid, which is routed to the sulfuric acid recovery unit. The crude TNT is purified in a similar manner as the batch process. Details on the TNT purification process are available.[4]

Although they are not the major emissions, SO_x and sulfuric acid mist are emitted in the manufacture of TNT. The principal sources of SO_x emissions are the vents from 1) nitration vessel acid fume collection and recovery systems, 2) sulfuric acid concentrators, and 3) water, sellite, and post-sellite purification washes. Of the three washes, the post-sellite wash is expected to produce the largest SO_x emission. Emissions of SO_x from the incineration of red water or the onsite production of oleum used in TNT production can also be considered significant. (Emissions from oleum or sulfuric acid manufacture are discussed in Section 5.5.)

5.10.1.2 Nitrocellulose (NC)--

Nitrocellulose can be prepared by either a batch-type "mechanical dipper" process, or a continuous process developed by Hercules, Inc. Both methods follow the same nitration and washing steps.[5,6] The overall reaction may be expressed as:

$$\underset{\text{Cellulose}}{C_6H_7O_2(OH)_3} + \underset{\substack{\text{Nitric}\\\text{acid}}}{3HNO_3} \xrightarrow{H_2SO_4} \underset{\text{Nitrocellulose}}{C_6H_7O_2(NO_3)_3} + \underset{\text{Water}}{3H_2O}$$

When nitration is complete, the reaction mixtures are centrifuged to remove most of the spent acid, which is fortified and reused or disposed of. The centrifuged NC undergoes a series of water washings and boiling treatments for purification.[7]

Principal sources of SO_x emissions from batch nitrocellulose manufacture are the vents from the reaction pots and centrifuges, spent acid concentrators, and boiling tubs used for purification.

5.10.1.3 Nitroglycerine (NG)--

Nitroglycerine is the principal explosive component in dynamite. The older batch method of production is gradually being replaced by the continuous Biazzi process.[8,9] In either case, glycerine is nitrated in the presence of sulfuric acid according to the following formula:

$$3HNO_3 + C_3\,H_8O_3 \quad {}^{H_2SO_4} \quad C_3H_5N_3O_9 + 3H_2O$$

Nitric acid Glycerine Nitroglycerine Water

Sulfur dioxide emissions from the absorber vent, the reactor, and washwater system are expected to be small.

5.10.2 Control Techniques

Liquid scrubbers and acid mist eliminators are the control devices reported to be used to reduce emissions of SO_x and sulfuric acid from production of TNT, NC, and NG.[10] The emissions being controlled are primarily those arising from the onsite recovery and regeneration of sulfuric acid and oleum. A flow scheme for sulfuric acid recycling is given in Figure 5.10-2.[11] Recovery systems such as acid fume recovery and spent acid recovery are usually found in the larger explosives manufacturing operations.[12] Both large and small producers reportedly discharge emissions from the purification and drying of TNT, NC, and NG directly to the atmosphere without treatment.

Producers of TNT at the Volunteer Army Ammunitions Plant (VAAP) in Chattanooga, Tennessee, used packed column water scrubbers to recover sulfuric acid from captured nitration process fumes and spent acid recovery exhausts.[13] Recovered sulfuric acid (68 percent) is converted first to SO_3,

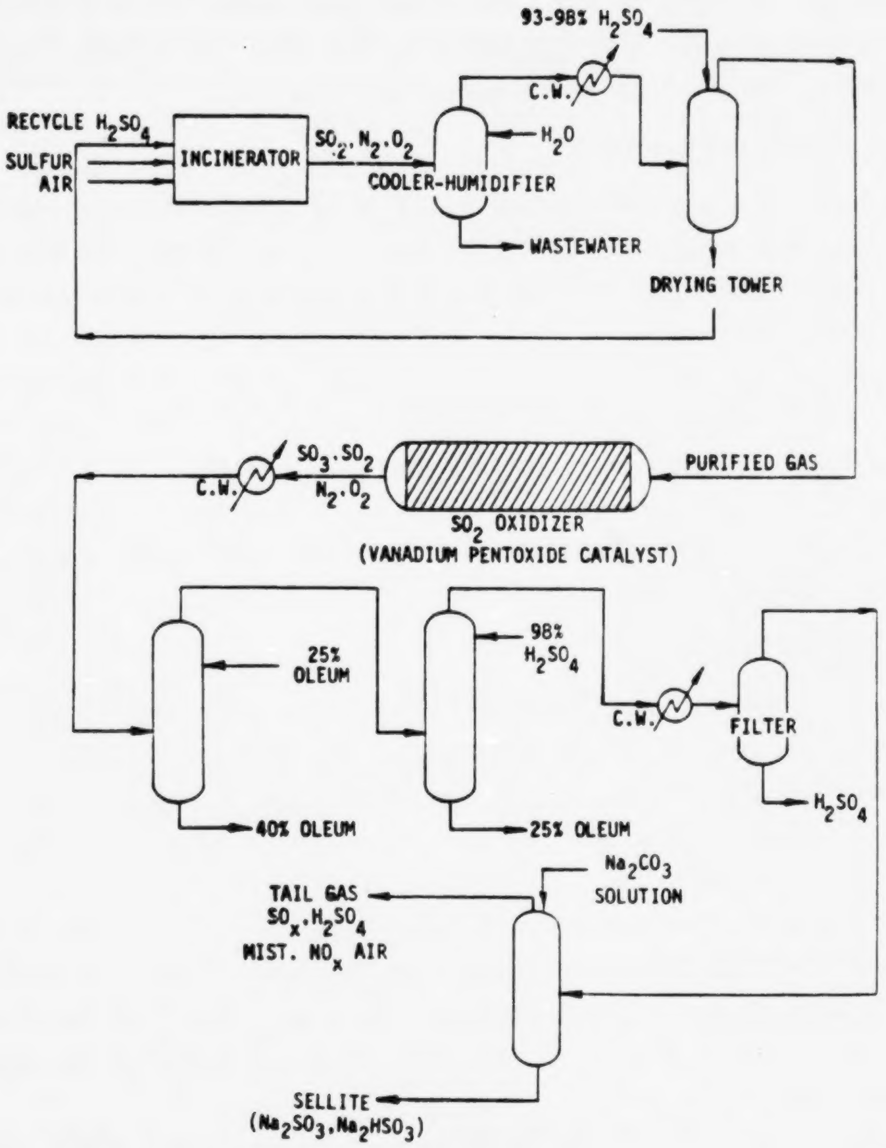

93-98% H_2SO_4
C.W.
RECYCLE H_2SO_4
SULFUR
AIR
INCINERATOR
SO_2, N_2, O_2
H_2O
COOLER-HUMIDIFIER
WASTEWATER
DRYING TOWER
SO_3, SO_2
N_2, O_2
C.W.
PURIFIED GAS
SO_2 OXIDIZER
(VANADIUM PENTOXIDE CATALYST)
25% OLEUM
98% H_2SO_4
C.W.
FILTER
40% OLEUM
25% OLEUM
H_2SO_4
Na_2CO_3 SOLUTION
TAIL GAS
SO_x, H_2SO_4
MIST, NO_x AIR
SELLITE
(Na_2SO_3, Na_2HSO_3)

Figure 5.10-2. Sulfur acid recycle system.[11]

then to oleum in a three-step regeneration process involving a rotary kiln, a vanadium catalyst, and a sulfuric acid/oleum scrubbing system. Sulfuric acid mist in the exhaust gas from the scrubber is removed by a Brinks mist eliminator. Residual SO_2 and SO_3 are scrubbed again, this time with a sodium carbonate (Na_2CO_3) solution, to produce a sellite solution of sodium sulfite (Na_2SO_3) and sodium bisulfite ($NaHSO_3$), which is recycled for use in TNT purification.

The final stack gas emission from the sulfuric acid recovery and regeneration system at VAAP is reported to contain 240 to 275 ppm SO_2, plus residual sulfuric acid mist. VAAP has indicated that the SO_x emission control system, as described above, is 95 percent efficient for both acid mist elimination and SO_2 removal.[14] VAAP officials plan to add a second mist eliminator behind the carbonate scrubber to remove the remaining acid mist.

Fluctuations in processing variables such as temperature and pressure changes within a system, breathing losses, process upsets or spills, and efficiency of absorbers towers can influence the efficiency of SO_x and acid mist controls. Table 5.10-1 presents 1975 data on control of SO_2 and acid mist emissions from the manufacture of TNT and NC.[15] More recent data are not available.

Information on costs, energy consumption, and environmental impacts of SO_x control devices in the explosives industry is not available in the open literature. Section 5.5 gives additional information on sulfuric acid processing, emissions, and control techniques.

TABLE 5.10-1. EMISSION FACTORS FOR MANUFACTURE OF TNT AND NC [15]

Type of process	Sulfur oxides[a] (SO_2)		Sulfuric acid mist[a] (100% H_2SO_4)	
	kg/Mg	lb/ton	kg/Mg	lb/ton
TNT: batch process				
Sulfuric acid concentrators				
Electrostatic precipitator (exit)	7 (2-20)	14 (4-40)	32.5 (0.5-94)	65 (1-188)
Electrostatic precipitator with scrubber	Negligible	Negligible	2.5 (2-3)	5 (4-6)
Red water incinerator				
Uncontrolled[b]	1 (0.025-1.75)	2 (0.05-3.5)		
Wet scrubber	1 (0.025-1.75)	2 (0.05-3.5)		
Sellite exhaust	29.5 (0.005-88)	59 (0.01-177)	3 (0.3-8)	6 (0.6-16)
TNT: continuous process				
Red water incinerator	0.12 (0.025-0.22)	0.24 (0.05-0.43)		
NC (nitrocellulose)				
Nitration reactors	0.7 (0.4-1)	1.4 (0.8-2)		
Sulfuric acid concentrator	34 (0.2-67)	68 (0.4-135)	0.3	0.3

[a] Considerable variations in emissions from some processes have been reported. The average of the values reported is shown first, with ranges in parentheses. Where only one value is given, it represents data from only one source test.

[b] Use low end of range for modern, efficient units and high end of range for older, less efficient units.

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12. Ref. 2, pp. 47, 52.
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5.11 PETROCHEMICALS

This section discusses sulfur oxide emissions from phthalic anhydride and ethylene production.

5.11.1 Process Description and Emission Sources

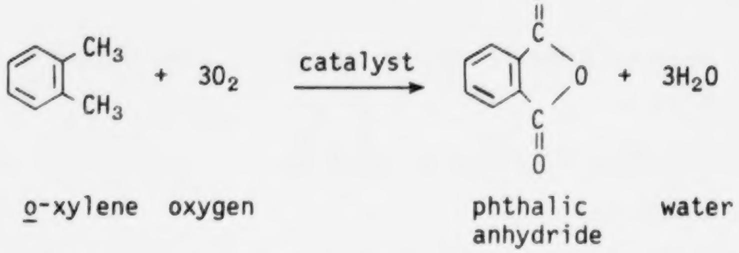
5.11.1.1 Phthalic Anhydride--

Phthalic anhydride is produced from either ortho-xylene or naphthalene by vapor phase oxidation in the presence of a vanadium oxide catalyst. In 1975, 10 phthalic anhydride plants were operating in the continental United States and 1 plant was operating in Puerto Rico. Nominal production capacity of the 11 plants was 495,000 Mg (544,000 tons) per year. Of this capacity, 70 percent (8 plants) used ortho-xylene as the feed stream, and the remainder relied on naphthalene. Plants representing another 208,000 Mg (229,000 tons) per year were not in operation. Of this capacity, all but 45,400 Mg (50,000 tons) was based on the use of naphthalene.[1] New plants are more likely to use the ortho-xylene process because the ortho-xylene feed is less expensive and has a higher yield ratio.

The two processes are similar except for the reactors used and the catalyst handling and recovery facilities. The naphthalene process uses fluidized-bed reactors that require catalyst recovery equipment to separate the entrained catalyst from the reactor effluent and return it to the fluidized bed. The ortho-xylene process uses fixed-bed tubular reactors. This process requires that 65 percent of the vanadium catalyst be in the tetravalent oxidation state, which is usually achieved by adding sulfur dioxide to the process airstream. A new ortho-xylene process has been developed by Rhone-Progil of France, and the process does not require catalyst regeneration with SO_2. Only one plant, however, is known to use this process.[2]

The catalyst regeneration step is not required in naphthalene-based plants;[3] consequently, so long as natural gas is used as fuel and the naphalene is sulfur free, these plants are not a source of SO_2 emissions.

The oxidation of ortho-xylene is carried out at 340° to 385°C (650° to 725°F).[4] The overall reaction is:



If uncontrolled, the reaction can proceed further than desired, and the phthalic anhydride product can be oxidized to maleic anhydride, or even to carbon dioxide and water.

In the ortho-xylene process, the feed is about 95 to 96 percent ortho-xylene, with the balance consisting of meta- and para-xylenes. The meta- and para-xylenes do not react to form acetic anhydride, but are oxidized to form carbon dioxide, carbon monoxide, and water. The ortho-xylene reaction produces benzoic acid and maleic anhydride as solid byproducts, which are emitted in significant amounts as particulates. Both of these are more volatile than phthalic anhydride.

Figure 5.11-1 is a flow diagram of the ortho-xylene process. At the start of the process, filtered air is compressed to between 69 and 97 kPa (10 to 14 psig) and is passed through a preheater. Liquid ortho-xylene is vaporized and mixed with the preheated air. The mixture of air and ortho-xylene then enters the reactor along with sulfur dioxide. The result is an exothermic reaction. Molten salt is circulated around the reactor tubes to draw off the heat, which is used to generate low-pressure steam.

The effluent from the reactor contains product phthalic anhydride, nitrogen, excess oxygen, carbon dioxide, carbon monoxide, water, and small amounts of maleic anhydride and benzoic acid. This effluent is passed to switch condensers to extract the solids. The effluent gas stream from the switch condenser, which contains SO_2, is usually scrubbed with water or incinerated before release to the atmosphere.[5]

The switch condensers are alternately cooled and heated by successive heat transfer oil streams. The time of the cycle is automatically controlled. Crude phthalic anhydride that has collected during the cold phase of the condenser cycle is melted from the condenser-tube fins during the hot-oil circulation period.

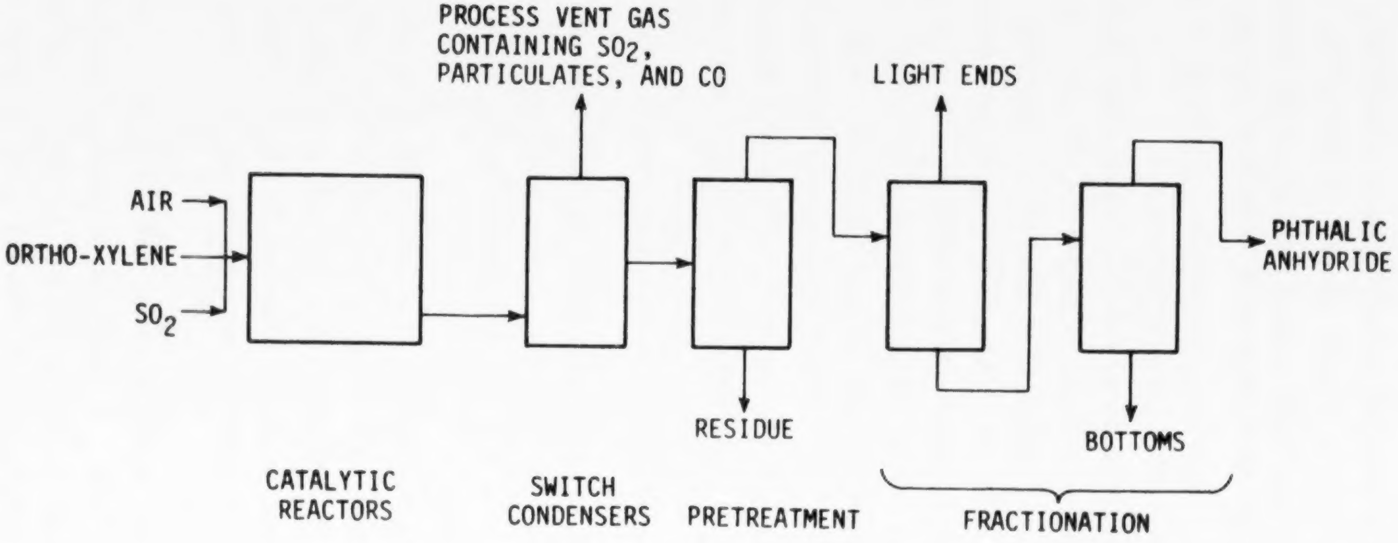

PROCESS VENT GAS CONTAINING SO_2, PARTICULATES, AND CO
LIGHT ENDS
AIR
ORTHO-XYLENE
SO_2
PHTHALIC ANHYDRIDE
RESIDUE
BOTTOMS
CATALYTIC REACTORS
SWITCH CONDENSERS
PRETREATMENT
FRACTIONATION

Figure 5.11-1. Ortho-xylene-based phthalic anhydride process.

Crude phthalic anhydride is then sent to the pretreatment section to be heated. Crude phthalic anhydride is dehydrated to form the pure anhydride. In this process, the associated water, maleic anhydride, and benzoic acid are partially evaporated. A liquid stream of anhydride is then sent to a vacuum distillation section where 99.8 percent pure phthalic anhydride is recovered. It can either be stored as a liquid or be solidified, converted to flakes, and bagged. The distillation residue consists of phthalic anhydride dissolved in nonvolatile organic compounds.

The sulfur dioxide used to maintain the vanadium catalyst in the tetravalent state is emitted in the gas vented from the process. This gas stream also contains significant amounts of carbon monoxide and organic particulates that must be controlled. A material balance, shown in Table 5.11-1, has been calculated for a plant with a yearly production capacity of 59 Gg (130 million lb). The values shown are for a discharge gas stream from a system with fresh catalyst and without pollution control equipment. If fresh catalyst is used, the sulfur dioxide content of the discharge gas stream is normally 135 ppm (by weight); with aged catalyst, sulfur dioxide levels can be two to three times higher (the normal upper limit is 400 ppm).[6]

5.11.1.2 Ethylene--

Ethylene is used to make polyethylene, ethylene dichloride, ethylene glycol, and other important products. Total production for 1979 is expected to be 13.2 Tg (29 billion lb), and the market is projected to grow at a rate of 6 to 7 percent per year.[7]

The choice of raw materials for ethylene production includes gases (such as ethane, propane, and butane) and petroleum refinery liquids (such as naphtha and gas oil). Although the production of ethylene from ethane is still the most important process, the use of liquid feeds is becoming more popular because they are becoming more available and allow the coproduction of gasoline and aromatics.

In ethylene plants using gaseous raw materials, natural gas is the primary source of the feed. A nearly pure ethane fraction is obtained when natural gas is processed in an amine unit to remove hydrogen sulfide and to separate the various components. A process flow diagram for the subsequent

TABLE 5.11-1. UNCONTROLLED GAS EMISSIONS VENTED FROM PHTHALIC ANHYRIDE PRODUCTION PROCESSES USING ORTHO-XYLENE AS FEED[a,b]

Component	Emissions, kg/h	(lb/h)	Ratio of emissions to product, by weight
Sulfur oxides	34	(75)	0.0047
Carbon monoxide	1,094	(2,411)	0.1507
Carbon dioxide	3,777	(8,326)	0.5204
Nitrogen	184,960	(407,760)	25.4850
Oxygen	46,240	(101,940)	6.3713
Phthalic anhydride	167	(368)	0.0230
Maleic anhydride	315	(694)	0.0434
Benzoic acid	20	(45)	0.0028
Water	6,955	(15,333)	0.9583
Total	243,563	(536,952)	33.5596

[a] Source: Reference 6.

[b] Plant capacity: 59 Gg (1.3×10^8 lb)/yr.

production of ethylene from ethane is shown in Figure 5.11-2. Propane and butane are converted to ethylene in a similar process. The only source of sulfur emissions from the production of ethylene is from sulfur impurities in the gas feed.

In the process shown, the gas stream is preheated before it is passed into the cracking furnace, where thermal decomposition takes place. The process typically takes place at a temperature of 857°C (1575°F) and a reactor residence time of less than 1 second.[7] The gas from the cracker is cooled in a fractionator by water scrubbing. A heavy gasoline is condensed in the fractionator along with some of the water.

Next, the gas stream is compressed and washed with aqueous sodium hydroxide to remove carbon dioxide and other impurities. Acetylene and other unsaturated hydrocarbons in the stream are then further converted to ethylene or saturated hydrocarbons. The next step involves drying and cooling of the stream to about -156°C (-250°F) and compression to about 3800 kPa (550 psi).[8] Hydrogen gas, which does not condense under these conditions, is removed.

The hydrocarbons are then separated by distillation into ethylene, ethane, and heavier hydrocarbons. Ethylene is the primary product; unconverted ethane is recycled; heavier hydrocarbons up to C_4 may either be recovered as product or used as fuel; and the C_5 hydrocarbon fraction is used in blending gasoline.

In plants producing ethylene from a liquid feed, hydrodesulfurization is required of gas oils and heavier fractions (which are particularly high in sulfur) prior to the introduction of the feed into the ethylene plant. Removal of sulfur from the feed is necessary to prevent the production of a cracked fuel oil with too high a sulfur content. The sulfur content of the raw feed is the only source of sulfur dioxide emissions in plants using a liquid feed.

A process flow diagram for the production of ethylene from liquid feeds is shown in Figure 5.11-3. The capital investment per kilogram (pound) of ethylene produced from liquid feeds is larger than that for ethane because the yield of ethylene from liquid feeds is less. It takes only 0.567 kg (1.25 lb) of ethane versus 1.42 kg (3.13 lb) of naphtha to produce 0.454 kg

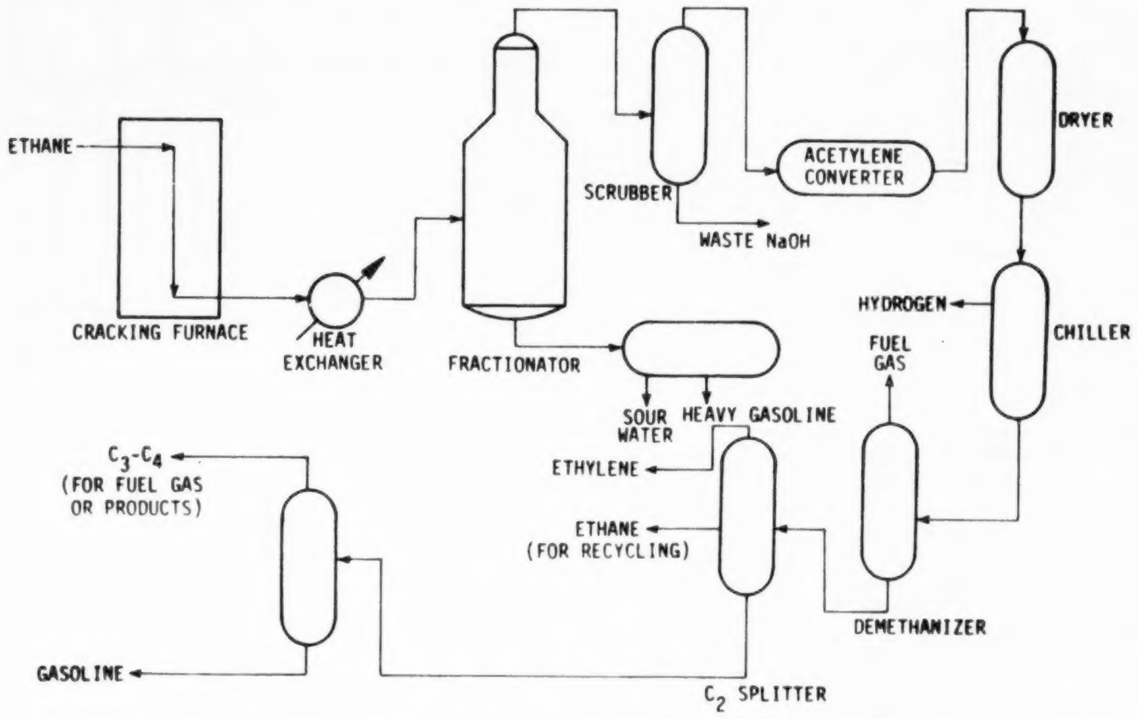

ETHANE
CRACKING FURNACE
HEAT EXCHANGER
FRACTIONATOR
SCRUBBER
WASTE NaOH
ACETYLENE CONVERTER
DRYER
CHILLER
HYDROGEN
FUEL GAS
SOUR WATER
HEAVY GASOLINE
ETHYLENE
ETHANE (FOR RECYCLING)
DEMETHANIZER
C_2 SPLITTER
C_3-C_4 (FOR FUEL GAS OR PRODUCTS)
GASOLINE

Figure 5.11-2. Ethylene from ethane.

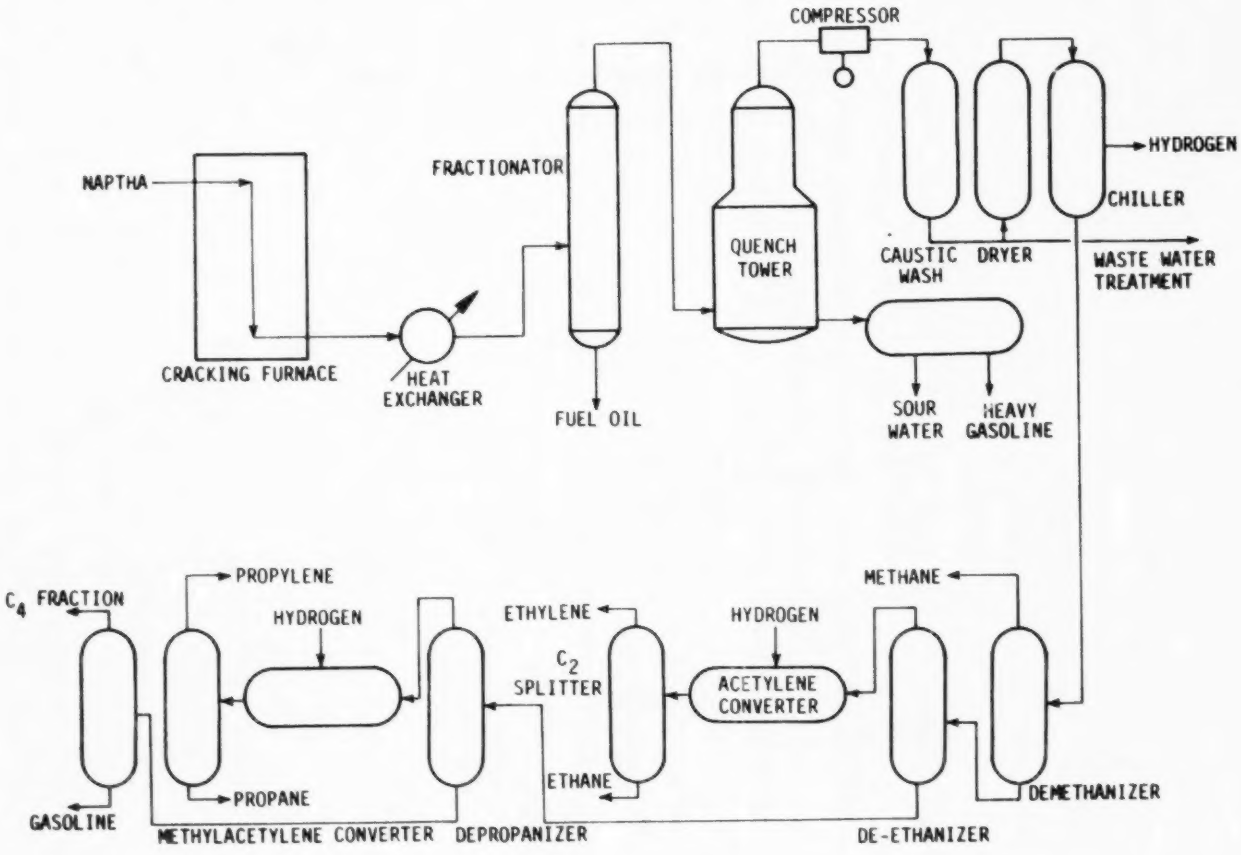

COMPRESSOR
NAPTHA
FRACTIONATOR
HYDROGEN
CHILLER
QUENCH TOWER
CAUSTIC WASH
DRYER
WASTE WATER TREATMENT
CRACKING FURNACE
HEAT EXCHANGER
FUEL OIL
SOUR WATER
HEAVY GASOLINE
PROPYLENE
METHANE
C_4 FRACTION
HYDROGEN
ETHYLENE
HYDROGEN
C_2 SPLITTER
ACETYLENE CONVERTER
ETHANE
PROPANE
DEMETHANIZER
GASOLINE
METHYLACETYLENE CONVERTER
DEPROPANIZER
DE-ETHANIZER

Figure 5.11-3. Ethylene from liquid feeds.

(1.0 lb) of ethylene.[9] The sale and disposition of byproducts is therefore important to offset the greater capital cost of processing liquid feeds.

The temperature and cracking furnace residence time used for processing liquids are similar to those used for gases. Somewhat higher steam pressures and temperatures are required to avoid fouling the heat exchanger surfaces with coke and pitch, and the coke deposits on the cracker must be burned off periodically. The combustion of this coke is a potential source of sulfur oxide emissions.

As in ethane processing, the feed stream is first preheated and then cracked. Rather than water, however, recirculated fuel oil is used for quenching. Fuel oil not required for quenching is recovered and sold. From the quench tower, heavy gasoline and sour water are removed.

The gas stream is compressed and washed with aqueous sodium hydroxide to remove impurities that may include sulfur compounds. The gases are then dried, cooled, and compressed. Hydrogen gas, which does not condense with the other gases, is removed for use elsewhere in the process. There are no atmospheric emissions of sulfur dioxide. An amine unit may be required to remove H_2S from the byproduct hydrogen.

The C_1 to C_4 hydrocarbons are separated by distillation. Ethylene, propylene, propane, and C_4 hydrocarbons are used as products; ethane is recycled to the process; and methylacetylene and other unsaturated hydrocarbons are converted to propylene and propane. The C_5 and higher hydrocarbons are used in blending gasoline.

Potential sources of sulfur emissions are the sour water removed with the heavy gasoline and the caustic solution used in washing the process gas stream prior to refrigeration. Sulfur compounds are removed from the sour water in a stripper. The sulfur-laden gases may be sent to a Claus unit for sulfur recovery or flared.

5.11.2 Control Techniques

5.11.2.1 Phthalic Anhydride--

The gas stream vented from ortho-xylene-based processes is the only source of sulfur dioxide emissions. All phthalic anhydride plants use pollution control devices on this stream to reduce emissions of organic species.[10] The control systems in use include water scrubber-incinerator combinations and incinerators.[11]

The water scrubber-incinerator removes organic particulate matter with a wet scrubber, and the liquid purge stream is subsequently incinerated. The carbon monoxide and sulfur dioxide vented from the scrubber are not controlled.

Direct incineration of the gas stream vented from the process controls both carbon monoxide and organic compounds, but again SO_2 emissions are uncontrolled.

Several methods are available for SO_2 control, but each has its disadvantages. If water-phase SO_2 controls are used, previous incineration will cause the following problems.

- The additional fuel (assuming natural gas) and air needed to ensure incineration dilutes the sulfur dioxide in the off-gas stream, which makes SO_2 scrubbing inefficient.
- The increase in the temperature of the gas stream from the incinerator increases the water requirements of the SO_2 scrubber.

Wet alkali scrubbing of the gas stream before incineration is not acceptable. In aqueous alkaline solution, phthalic and maleic anhydrides react as readily as sulfur dioxide and would be converted to salts. The sodium, potassium, and calcium salts of phthalic and maleic acid are water soluble and would appear in waste streams.

Because SO_2 emissions are greatest late in the life of the catalyst, one SO_2 control strategy is to regenerate or replace the catalyst more frequently. Catalyst replacement may be attractive if more frequent shutdowns and higher catalyst costs are economically feasible.

Rhone-Progil in France has developed a different process for producing phthalic anhydride from ortho-xylene. A commercial plant in France using this process has been in operation since 1971. The catalyst used does not require regeneration by SO_2. It has not been established, however, whether this catalyst is compatible with existing domestic plants.[2] Researchers at the French plant suggest that it may be possible to develop a catalyst that can be used in existing U.S. ortho-xylene plants and that does not require the addition of sulfur dioxide or other sulfur compounds.[2] Research in developing new catalysts and improving present catalysts is being conducted in the United States, mostly by private industry. Because the work is financed by the industries themselves, progress reports and research results are not disseminated. Consequently, it is not possible to determine the amount of research being conducted or the status of developments.

5.11.2.2 Ethylene--

Sulfur dioxide emissions within an ethylene plant are primarily controlled by removing the sulfur compounds from the feed streams. When gases are used as the feed, the hydrogen sulfide in the natural gas stream is absorbed in an amine solution and then processed into elemental sulfur or sulfuric acid. A more detailed discussion is presented in Section 5.4, Natural Gas Industry. If gas oils are the feed source, it is necessary to remove the sulfur through hydrodesulfurization. A hydrogen sulfide stream from the desulfurization process is then converted to elemental sulfur. A more detailed discussion of this process is presented in Section 5.3, Petroleum Refineries.

In ethylene plant feeds containing significant amounts of sulfur, potential emission sources are the sour water coproduced with the heavy gasoline and the sulfur dioxide produced by burning coke deposits from heat exchanger surfaces during maintenance periods.

Sulfur is disposed of in several ways. Sulfur stripped from the sour water in the form of hydrogen sulfide is either converted to elemental sulfur in a Claus plant or incinerated to form sulfur dioxide, which is released to the atmosphere. Sulfur dioxide emissions from the burning of coke deposits are also released to the atmosphere.

Specific plant operating procedures can be followed to reduce the buildup of coke on the furnace tubes and thus minimize SO_2 emissions from decoking operations. Control costs and environmental impacts of removing sulfur from natural gas and heavy gas oils are discussed in other sections of this report.

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5.12 INCINERATION

5.12.1 Process Descriptions and Emission Sources

Municipal and offsite incinerators are large, centrally located combustion systems that are designed to handle a variety of wastes. Municipal incinerators burn a mixture of residential, commercial, and industrial solid wastes. Private offsite incinerators may be designed to handle liquid, solid, and sludge wastes, especially those generated by industry.[1]

Municipal incinerator capacities range from 45 to 90 Mg (50 to 100 tons) per day for smaller units to more than 900 Mg (1000 tons) per day for larger installations.[2] Most municipal incinerators operate continuously, and use little or no auxiliary fuel. Details of design and operation are available from several sources.[3-5]

In contrast to the large municipal incinerators, smaller sized incinerators that handle industrial, commercial, domestic, institutional, or pathological wastes are usually located near the point of the waste generation. For this reason they are often referred to as onsite incinerators. Nine out of ten are multichambered, operate up to 8 hours a day, have intermediate-sized capacities of 450 kg/h (1000 lb/h) or less, and utilize auxiliary fuel (especially natural gas).[6-8]

Incineration is also an effective technique for sewage sludge disposal. Sludge incineration systems usually include a sludge pretreatment stage to thicken and dewater the incoming sludge.[9] Auxiliary fuel may be required during startup or when the sludge cannot support combustion as a result of moisture content.[9,10]

The major emission point from an incinerator is the furnace stack, and the only pollutant typically controlled is particulate matter. Sulfur oxide emissions occur at relatively low levels compared with other pollutants.[11-13] Studies have shown that sulfur dioxide (SO_2) emissions appear to be more dependent upon the sulfur content of the incoming waste than upon operating conditions associated with the burning process.[14-16]

On the average, municipal refuse contains about 0.1 percent sulfur.[17] Sulfur compounds, usually in the form of sulfates and sulfides, are present chiefly in paper, food waste, garden waste, and rubber. During incineration, some of these compounds are converted to SO_2 and possibly some SO_3.[18]

Based on the assumptions of the average sulfur value for refuse composition and total conversion to SO_2, it was estimated in 1970 that the SO_2 emission factor was 2 kg/Mg (4 lb/ton) refuse fired.[19] Another estimate placed the value between 0.5 and 0.9 kg/Mg (1 and 2 lb/ton) refuse fired.[17] These values agree reasonably well with SO_2 emission rates measured at 13 municipal incinerators; the average value reported was 1.2 kg SO_2/Mg (2.3 lb/ton) refuse, with a standard deviation of 0.8 kg/Mg (1.8 lb/ton).[19] In a similar study from 1968 to 1969, four New York City incinerators were monitored for SO_2 emissions. Reported values ranged from 0.6 to 2.9 kg/Mg (1.3 to 5.8 lb/ton) refuse, with an overall average of 1.5 kg/Mg (3.0 lb/ton).[20]

Another municipal incinerator study recently found SO_2 emissions ranging from 17 to 120 parts per million (ppm) with an average concentration of 66 ppm over a 3-day test period.[21] These values are compared with the ppm SO_2 values obtained in the earlier New York study mentioned above and with data from several other studies.[22]

Sulfur oxide emissions from refuse incinerators represent only a fraction of a percent of total national sulfur oxide emissions. It was estimated that total SO_2 emissions from municipal incinerators in 1977 were 6.2 Gg (7300 tons) compared with 17.2 Gg (19,000 tons) for onsite incinerators.[23] These values may have been on the conservative side because they were based on an emission factor of 0.75 kg of SO_2 per Mg (1.5 lb/ton) refuse. Table 5.12-1 lists sulfur oxide emission factors for various types of refuse incinerators.[24]

The average sulfur content of sewage sludges is about 1 to 2 percent.[9,25] Much of this sulfur is in the form of sulfates or other stable compounds and is not converted to SO_2 during incineration. Emissions measured at several incinerators were less than 750 g of SO_2 per Mg (1.5 lb of SO_2 per ton) of sludge burned.[25] Average SO_2 emission concentrations are under 14 ppm.[26]

5.12.2 Control Techniques

Nearly all incinerators are equipped with some type of particulate control equipment; i.e., afterburners, settling chambers, water sprays/scrubbers, electrostatic precipitators.[4,27] Primary sulfur oxide emission

TABLE 5.12-1. SULFUR OXIDE EMISSION FACTORS FOR REFUSE INCINERATORS[24]

Incinerator type	Sulfur oxides as SO_2, kg/Mg (lb/ton)
Municipal	
Multiple chamber, uncontrolled	1.25 (2.5)
With settling chamber and water spray system	1.25 (2.5)
Industrial/commercial	
Multiple chamber	1.25 (2.5)
Single chamber	1.25 (2.5)
Domestic	
Flue-fed, single chamber	0.25 (0.5)
Flue-fed with afterburners and draft controls	0.25 (0.5)
Single chamber with or without primary burner	0.25 (0.5)
Pathological	Negligible
Open burning/trench	
Wood	0.05 (0.1)
Rubber tires	N.A.[a]
Municipal refuse	1.25 (2.5)
Auto body	NA

[a] NA - Not available.

control is not practiced, and gaseous SO_x emissions from incineration apparently are unaffected by the particulate control systems with one exception. There is some evidence that wet scrubbers used for particulate control from sludge incineration may also remove about 20 percent of the SO_2.[28] Higher SO_2 removal efficiencies have apparently been realized in one sludge incineration system utilizing a fluidized-bed incinerator with a venturi scrubber having a 4.5 kPa (18 in. water) pressure drop.[29] See Table 5.12-2 for details. The use of venturi scrubbers on municipal incinerators is expected to decrease because the device has not generally been successful in meeting the New Source Performance Standards (NSPS) for particulate matter.[30] Because venturi scrubbers have successfully met emission standards for sludge incinerators, however, their use in this type of incineration process is expected to continue.[31]

5.12.3 Control Costs

Cost figures for SO_x emission control are not available because it is not practiced today in incineration.

5.12.4 Energy and Environmental Impact

Impacts are not available because control of sulfur oxides is not typically practiced.

TABLE 5.12-2. SO_2 EMISSIONS FROM CONTROLLED SEWAGE SLUDGE INCINERATORS[26]

Facility[a]	SO_2 emissions from stack effluent, ppm				Total particulate emissions, average kg/Mg feed (lb/ton)
	Run 1	Run 2	Run 3	Average	
A	< 0.3	< 0.3	< 0.3	< 0.3	0.35 (0.704)
B	2.29-2.57	2.75		2.53	1.96 (3.94)
C	11.9-15.9	14.5-14.6	13.3-14.6	14.2	1.63 (3.23)
D	8.29-11.2	14.8	14.2-15.4	13.8	1.63 (3.24)
E	2.01	2.07	2.12	2.07	1.89 (3.72)

[a] A: Fluidized-bed, 500 kg/h (1100 lb/h) dry solids capacity, 100% capacity operation during test, venturi scrubber with 4.5 kPa (18 in.) water pressure drop.

B: Multiple-hearth (six hearths) Herreschoff incinerator, 3.40 kg/h (750 lb/h) dry solids capacity, 64% capacity operation during test, single cross-flow perforated plate impinjet scrubber with a 1.5 kPa (6.0 in.) water pressure drop.

C: Multiple-hearth (six hearths) Herreschoff incinerator, 408 kg/h (900 lb/h) dry solids capacity, 35% capacity operation during test, single cross-flow perforated plate impinjet scrubber with a 1.5 kPa (6.0 in.) water pressure drop.

D: Fluidized bed, 226 kg/h (500 lb/h) dry solids capacity, 95% capacity operation during test, single cross-flow perforated plate impinjet scrubber with 1.0 kPa (4.0 in.) water pressure drop.

E: Multiple-hearth Herreschoff incinerator, 1134 kg/h (2500 lb/h) dry solids capacity, 50% capacity operation during test, cyclonic inertial jet scrubber with 0.6 kPa (2.5 in.) water pressure drop.

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TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-450/3-81-004	2.	3. RECIPIENT'S ACCESSION NO.
4. TITLE AND SUBTITLE Control Techniques for Sulfur Oxide Emissions From Stationary Sources - Second Edition		5. REPORT DATE
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, North Carolina 27711		10. PROGRAM ELEMENT NO.
		11. CONTRACT/GRANT NO. PN 3450-7 68-02-3173 (Task 7) PEDCo Environmental
12. SPONSORING AGENCY NAME AND ADDRESS DAA for Air Quality Planning and Standards Office of Air, Noise, and Radiation U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711		13. TYPE OF REPORT AND PERIOD COVERED
		14. SPONSORING AGENCY CODE EPA 200/04

15. SUPPLEMENTARY NOTES

This document is issued per the requirements of Section 108 of the Clean Air Act Amendments of 1977

16. ABSTRACT

Control Techniques for Sulfur Oxide Emissions From Stationary Sources presents recent developments of control techniques which have become available since preparation of the first edition of Control Techniques for Sulfur Oxide Air Pollutants (AP-52). This edition presents available data on characterization and sampling methods for sulfur oxides, descriptions of stationary sources of sulfur oxides and control techniques used to reduce sulfur oxide emissions. Control costs and energy and environmental impact of controlling sulfur oxide emissions are also discussed.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Sulfur Oxides Control Techniques Combustion Processes Emission Control Costs Industrial Processes		13 B

18. DISTRIBUTION STATEMENT Unlimited	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 558
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

United States
Environmental Protection
Agency

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